Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Palladium(II)-Catalyzed 1,3-Heteroaryl Acyloxylation of Propargylic Electrophiles

Shenghan Teng,‡ Peiyao Liang,‡ Lin Hu, Siyi Chen, Shoulei Wang,* Wei Huang**

Procedures and characterization of compounds

Table of contents

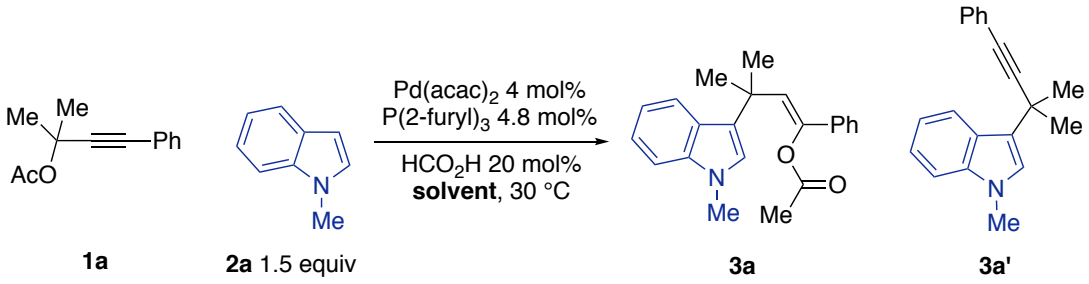
I. General

^{1}H, ^{13}C and ^{19}F NMR spectra were acquired on Joel (600 MHz) or Bruker (400 MHz) instruments in indicated deuterated solvents. ^{1}H NMR chemical shifts were recorded relative to residual protic solvents ($CDCl_3$: δ 7.26). Multiplicities were given as: s (singlet), d (doublet), t (triplet), q (quartet) and m (multiplet). The number of protons (n) for a given resonance was indicated by nH. Coupling constants were reported as a *J* value in Hz. ^{13}C NMR chemical shifts were recorded relative to solvent resonance ($CDCl_3$: δ 77.16, CD_3CN: δ 118.26 ± 0.02, 1.32 ± 0.02). ^{19}F NMR chemical shifts were uncorrected.

Unless noted otherwise, commercially available chemicals and solvents were used as received without purification. Flash chromatography was packed with silica gel as the stationary phase. High resolution mass spectra (HRMS) were recorded on a Waters G2-XS QTof spectrometer with ESI mode unless otherwise stated.

II. Optimization of conditions

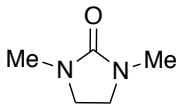
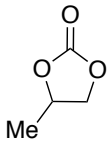
General procedure for solvent screening: in an argon-filled glovebox, $Pd(acac)_2$ (1.2 mg, 0.004 mmol), P(2-furyl)$_3$ (1.1 mg, 0.0048 mmol) and 0.1 mL of solvent were charged into an oven-dried 4-mL vial. After stirring for about 15 minutes at rt, *N*-methylindole (19 μL, 0.15 mmol), formic acid (0.8 μL, 0.02 mmol) and propargylic acetate **1a** (20.2 mg, 0.1 mmol) were added sequentially to the reaction mixture. The vial was sealed with a screw cap and placed in a heating block maintained at 30 °C. After stirring for 24 hours, the reaction mixture was directly evaporated under the reduced pressure. The crude product was then subjected to ^{1}H NMR to determine the conversion and yield using 1,3,5-trimethoxybenzene as the internal standard.



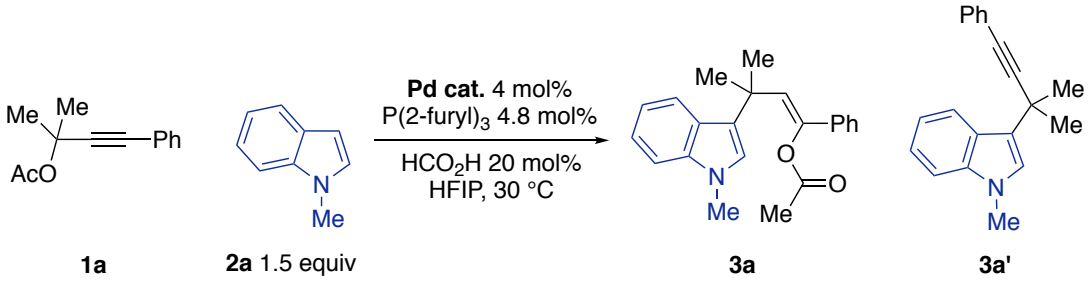
1a **2a** 1.5 equiv **3a** **3a'**

Table S1. Solvent screening

entry	solvent	conversion of **1a**	yield of **3a** (Z/E)	yield of **3a′**
1	DCM	42%	0%	0%
2	toluene	41%	0%	0%
3	MTBE	39%	0%	0%
4	DME	14%	0%	0%
5	1,4-dioxane	24%	0%	0%
6	MeCN	28%	0%	0%
7	DMF	16%	0%	0%

8		20%	0%	0%
9	DMSO	58%	0%	0%
10		60%	0%	0%
11	MeOH	66%	0%	0%
12	*i*-PrOH	28%	0%	0%
13	*t*-BuOH	14%	0%	0%
14	CF_3CH_2OH	100%	77% (>20:1)	0%
15	$(CF_3)_2CHOH$	100%	86% (>20:1)	0%

General procedure for the studies of Pd catalysts: in an argon-filled glovebox, palladium catalyst (0.004 mmol), P(2-furyl)$_3$ (1.1 mg, 0.0048 mmol) and 0.1 mL of 1,1,1,3,3,3-hexafluoroisopropanol (HFIP) were charged into an oven-dried 4-mL vial. After stirring for about 15 minutes at rt, *N*-methylindole (19 μL, 0.15 mmol), formic acid (0.8 μL, 0.02 mmol) and propargylic acetate **1a** (20.2 mg, 0.1 mmol) were added sequentially to the reaction mixture. The vial was sealed with a screw cap and placed in a heating block maintained at 30 °C. After stirring for 24 hours, the reaction mixture was directly evaporated under the reduced pressure. The crude product was then subjected to ^{1}H NMR to determine the conversion and yield using CH_2Br_2 as the internal standard.

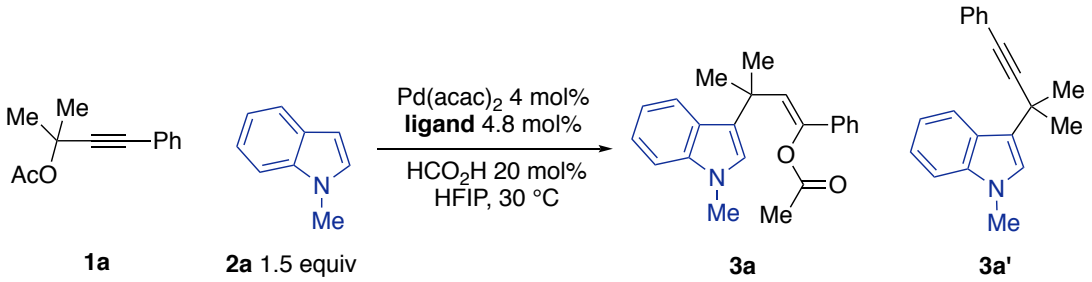


1a **2a** 1.5 equiv **3a** **3a'**

Table S2. The effect of palladium source

entry	Pd catalyst	conversion of **1a**	yield of **3a**	yield of **3a′**
1	$PdCl_2$	100%	0%	27%
2	$Pd(OAc)_2$	100%	19%	3%
3	$Pd(TFA)_2$	100%	63%	0%
4	$Pd(acac)_2$	100%	86%	0%
5	$Pd(hfacac)_2$	100%	72%	0%
6	$Pd(cod)Cl_2$	100%	79%	0%
7	$Pd(MeCN)Cl_2$	100%	79%	0%
8	$Pd(PPh_3)_4$	95%	0%	22%
9	$Pd(dba)_2$	100%	13%	20%

General procedure for the studies of phosphine ligands: in an argon-filled glovebox, $Pd(acac)_2$ (1.2 mg, 0.004 mmol), phosphine ligand (0.0048 mmol) and 0.1 mL of HFIP were charged into an oven-dried 4-mL vial. After stirring for about 15 minutes at rt, *N*-methylindole (19 μL, 0.15 mmol), formic acid (0.8 μL, 0.02 mmol) and propargylic acetate **1a** (20.2 mg, 0.1 mmol) were added sequentially to the reaction mixture. The vial was sealed with a screw cap and placed in a heating block maintained at 30 °C. After stirring for 24 hours, the reaction mixture was directly evaporated under the reduced pressure. The crude product was then subjected to ^{1}H NMR to determine the conversion and yield using 1,3,5-trimethoxybenzene as the internal standard.



1a **2a** 1.5 equiv **3a** **3a'**

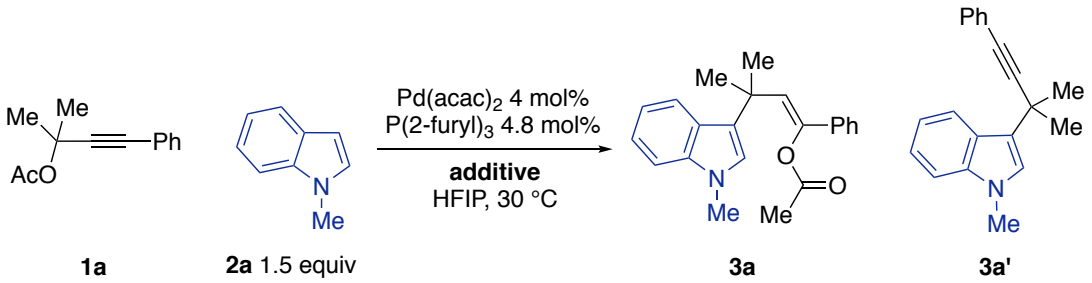
Table S3. The effect of phosphine ligands

entry	ligand	conversion of **1a**	yield of **3a** (Z/E)	yield of **3a′**
1	P(2-furyl)$_3$	100%	86% (>20:1)	0%
2	P(2-thiophenyl)$_3$	100%	51% (5:1)	25%
3	PPh_3	100%	0%	19%
4	P(4-MeOC$_6$H$_4$)$_3$	100%	32% (1.2:1)	18%
5	PCy_3	100%	49% (10:1)	29%
6	bpy	97%	0%	11%
7	phen	96%	0%	12%

General procedure for the studies of additives: in an argon-filled glove box, $Pd(acac)_2$ (24.5 mg, 0.08 mmol), P(2-furyl)$_3$ (22.3 mg, 0.096 mmol) and 2 mL of $(CF_3)_2CHOH$ were charged into an oven-dried 8-mL vial. After stirring for about 30 minutes at rt, the yellow solution of Pd complex was ready for use.

To another oven-dried 4-mL vial, 0.1 mL of the Pd complex (0.004 mmol, 4 mol%) from the stock solution was added under argon, followed by the sequential addition of *N*-methylindole (19 μL, 0.15 mmol), the additive and propargylic acetate (20.2 mg, 0.1 mmol). The vial was sealed with a screw cap and placed in a heating block maintained at 30 °C. After stirring for 24 hours, the reaction mixture was directly evaporated under the reduced pressure. The crude product was then subjected to ^{1}H NMR to determine the conversion and yield using CH_2Br_2 as the internal standard.

Result: Formic acid (20 mol%) was needed to afford the desired product in the optimal yield (84%). Furthermore, the prepared Pd complex (4 mol%) provided the same result as the in-situ generated Pd catalyst in this reaction.



1a **2a** 1.5 equiv **3a** **3a'**

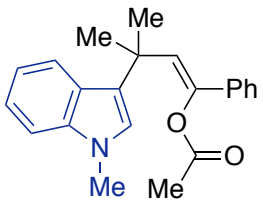
Table S4. The influence of additives

entry	additive	conversion of **1a**	yield of **3a**	yield of **3a′**
1	HCO_2Na (1.2 equiv)	100%	51%	13%
2	HCO_2K (1.2 equiv)	100%	66%	16%
3	HCO_2NH_4 (1.2 equiv)	100%	47%	31%
4	HCO_2H (1.2 equiv)	100%	86%	0%
5	HCO_2H (20 mol%)	100%	86%	0%
6	$PhCO_2H$ (20 mol%)	100%	65%	0%
7	$TsOH·H_2O$ (20 mol%)	100%	71%	8%
8	AcOH (20 mol%)	100%	49%	25%
9	PivOH (20 mol%)	100%	38%	8%
10	none	100%	54%	20%

III. General procedure for 1,3-heteroaryl acyloxylation of propargylic electrophiles

(A) The procedure for reactions in the scope of heteroarenes: Unless otherwise stated, the procedure was as follows. In an argon-filled glove box, $Pd(acac)_2$ (24.5 mg, 0.08 mmol), $P(2\text{-furyl})_3$ (22.3 mg, 0.096 mmol) and 2 mL of $(CF_3)_2CHOH$ were charged into an oven-dried 8-mL vial. After stirring for about 30 minutes at rt, the yellow solution of Pd complex was ready for use.

To another oven-dried 4-mL vial, 0.1 mL of the Pd complex (0.004 mmol, 4 mol%) from the stock solution was added under argon, followed by the sequential addition of heteroarene (0.15 mmol), formic acid (0.8 μL, 0.02 mmol) and propargylic acetate **1a** (20.2 mg, 0.1 mmol). The vial was sealed with a screw cap and placed in a heating block maintained at 30 °C. After stirring for 24 hours, the crude reaction mixture was purified by flash chromatography on silica using ethyl acetate/hexanes as eluent.



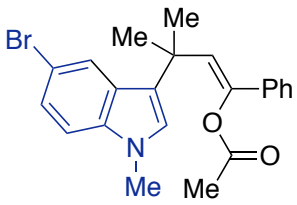
(*Z*)-3-Methyl-3-(1-methyl-1*H*-indol-3-yl)-1-phenylbut-1-en-1-yl acetate (3a)

The product was isolated by flash chromatography (ethyl acetate/hexanes 1:20) as yellow oil. 29 mg, 86% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (d, *J* = 8.0 Hz, 1H), 7.35-7.33 (m, 2H), 7.28-7.17 (m, 5H), 7.05 (t, *J* = 7.1 Hz, 1H), 6.84 (s, 1H), 5.99 (s, 1H), 3.72 (s, 3H), 1.87 (s, 3H), 1.65 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 169.0, 145.1, 137.8, 136.6, 128.5, 128.1, 126.7, 126.5, 124.8, 124.5, 123.7, 121.5, 121.2, 118.8, 109.3, 35.9, 32.7, 29.2, 20.6.

HRMS (ESI): Calcd for $C_{22}H_{23}NO_2Na$ $[M+Na]^+$: 356.1626; found: 356.1620.



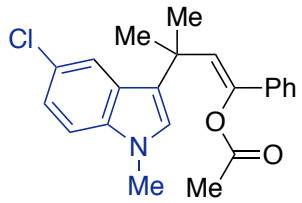
(*Z*)-3-(5-Bromo-1-methyl-1*H*-indol-3-yl)-3-methyl-1-phenylbut-1-en-1-yl acetate (3b)

The product was isolated by flash chromatography (ethyl acetate/hexanes 1:10) as yellow oil. 29 mg, 71% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (d, *J* = 1.9 Hz, 1H), 7.38 (d, *J* = 6.8 Hz, 2H), 7.33-7.24 (m, 4H), 7.16 (d, *J* = 8.7 Hz, 2H), 5.95 (s, 1H), 3.73 (s, 3H), 1.88 (s, 3H), 1.65 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 168.9, 145.4, 136.4, 128.6, 128.3, 128.2, 125.93, 125.88, 124.9, 124.4, 123.6, 123.2, 112.3, 110.8, 35.8, 32.8, 29.4, 20.5.

HRMS (ESI): Calcd for $C_{22}H_{22}{}^{79}BrNO_2Na$ $[M+Na]^+$: 434.0726; found: 434.0729.



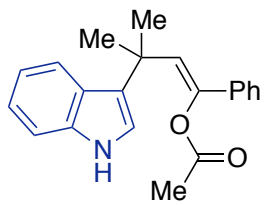
(*Z*)-3-(5-Chloro-1-methyl-1*H*-indol-3-yl)-3-methyl-1-phenylbut-1-en-1-yl acetate (3c)

The product was isolated by flash chromatography (ethyl acetate/hexanes 1:10) as yellow oil. 30 mg, 81% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (d, *J* = 1.9 Hz, 1H), 7.34 (d, *J* = 6.8 Hz, 2H), 7.29-7.22 (m, 3H), 7.18-7.12 (m, 2H), 6.86 (s, 1H), 5.92 (s, 1H), 3.70 (s, 3H), 1.84 (s, 3H), 1.62 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 168.9, 145.4, 136.4, 136.2, 128.6, 128.2, 127.6, 126.0, 125.9, 124.9, 124.6, 123.2, 121.8, 120.6, 110.3, 35.8, 32.9, 29.4, 20.5.

HRMS (ESI): Calcd for $C_{22}H_{22}ClNO_2Na$ $[M+Na]^+$: 390.1237; found: 390.1242.



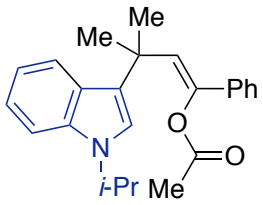
(*Z*)-3-(1*H*-Indol-3-yl)-3-methyl-1-phenylbut-1-en-1-yl acetate (3d)

The product was isolated by flash chromatography (ethyl acetate/hexanes 1:8) as yellow oil. 30 mg, 95% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (s, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.39-7.34 (m, 3H), 7.32-7.25 (m, 3H), 7.19 (t, *J* = 7.2 Hz, 1H), 7.10 (t, *J* = 7.2 Hz, 1H), 7.00 (d, *J* = 2.4 Hz, 1H), 6.04 (s, 1H), 1.89 (s, 3H), 1.69 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 169.1, 145.3, 137.1, 136.5, 128.6, 128.1, 126.32, 126.29, 125.2, 124.8, 121.9, 121.2, 119.6, 119.3, 111.3, 35.8, 29.2, 20.6.

HRMS (ESI): Calcd for $C_{21}H_{21}NO_2Na$ $[M+Na]^+$: 342.1470; found: 342.1479.



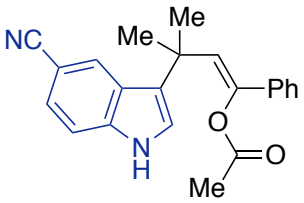
(*Z*)-3-(1-Isopropyl-1*H*-indol-3-yl)-3-methyl-1-phenylbut-1-en-1-yl acetate (3e)

The product was isolated by flash chromatography (ethyl acetate/hexanes 1:20) as yellow oil. 31 mg, 86% yield.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.80 (d, *J* = 8.0 Hz, 1H), 7.40-7.37 (m, 3H), 7.32-7.29 (m, 2H), 7.27-7.25 (m, 1H), 7.21 (t, *J* = 7.6 Hz, 1H), 7.09 (t, *J* = 7.5 Hz, 1H), 7.05 (s, 1H), 6.06 (s, 1H), 4.68 (hept, *J* = 6.7 Hz, 1H), 1.91 (s, 3H), 1.70 (s, 6H), 1.54 (d, *J* = 6.7 Hz, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 169.0, 145.1, 136.62, 136.60, 128.5, 128.0, 126.8, 126.6, 124.8, 123.7, 121.3, 121.1, 119.0, 118.7, 109.5, 46.9, 36.0, 29.3, 22.9, 20.7.

HRMS (ESI): Calcd for $C_{24}H_{27}NO_2Na$ $[M+Na]^+$: 384.1934; found: 384.1935.



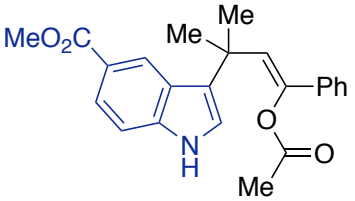
(*Z*)-3-(5-Cyano-1*H*-indol-3-yl)-3-methyl-1-phenylbut-1-en-1-yl acetate (3f)

The product was isolated by flash chromatography (ethyl acetate/hexanes 1:5) as yellow oil. 23 mg, 68% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.38 (s, 1H), 8.12 (s, 1H), 7.38-7.27 (m, 7H), 7.12 (d, *J* = 2.4 Hz, 1H), 5.96 (s, 1H), 1.81 (s, 3H), 1.65 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 168.8, 145.9, 138.8, 136.0, 128.7, 128.5, 126.8, 126.2, 126.0, 125.3, 124.90, 124.86, 121.8, 121.1, 112.2, 102.4, 35.6, 29.5, 20.5.

HRMS (ESI): Calcd for $C_{22}H_{20}N_2O_2Na$ $[M+Na]^+$: 367.1417; found: 367.1418.



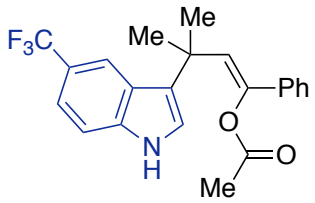
Methyl (*Z*)-3-(4-acetoxy-2-methyl-4-phenylbut-3-en-2-yl)-1*H*-indole-5-carboxylate (3g)

The product was isolated by flash chromatography (ethyl acetate/hexanes 1:5) as yellow oil. 34 mg, 89% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.56 (s, 1H), 8.29 (s, 1H), 7.81 (d, J = 8.6 Hz, 1H), 7.30 (d, J = 6.8 Hz, 2H), 7.26-7.17 (m, 4H), 6.98 (d, J = 2.5 Hz, 1H), 6.00 (s, 1H), 3.89 (s, 3H), 1.82 (s, 3H), 1.68 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 168.9, 168.4, 145.7, 139.8, 136.4, 128.6, 128.2, 126.2, 126.0, 125.9, 125.0, 124.1, 123.3, 121.4, 121.1, 111.0, 51.9, 35.8, 29.6, 20.5.

HRMS (ESI): Calcd for $C_{23}H_{23}NO_4Na$ $[M+Na]^+$: 400.1519; found: 400.1519.



(*Z*)-3-Methyl-1-phenyl-3-[5-(trifluoromethyl)-1*H*-indol-3-yl]but-1-en-1-yl acetate (3h)

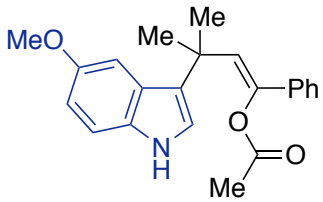
The product was isolated by flash chromatography (ethyl acetate/hexanes 1:10) as yellow oil. 29 mg, 75% yield.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.20 (s, 1H), 8.12 (s, 1H), 7.42-7.36 (m, 4H), 7.31-7.25 (m, 3H), 7.09 (d, J = 2.2 Hz, 1H), 5.95 (s, 1H), 1.86 (s, 3H), 1.68 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 169.0, 145.7, 138.5 (q, J_{CF} = 1.2 Hz), 136.5, 128.6, 128.3, 125.9, 125.8, 125.7, 125.6 (q, J_{CF} = 271.7 Hz), 125.0, 121.7 (q, J_{CF} = 31.5 Hz), 121.4, 118.8 (q, J_{CF} = 4.5 Hz), 118.7 (q, J_{CF} = 3.5 Hz), 111.5, 35.8, 29.4, 20.5.

^{19}F NMR (564.9 MHz, $CDCl_3$): δ -60.0.

HRMS (ESI): Calcd for $C_{22}H_{20}F_3NO_2Na$ $[M+Na]^+$: 410.1338; found: 410.1342.



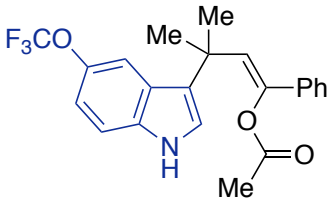
(*Z*)-3-(5-Methoxy-1*H*-indol-3-yl)-3-methyl-1-phenylbut-1-en-1-yl acetate (3i)

The product was isolated by flash chromatography (ethyl acetate/hexanes 1:10) as brown oil. 25 mg, 72% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (s, 1H), 7.38-7.36 (m, 2H), 7.31-7.20 (m, 5H), 6.96 (d, J = 2.4 Hz, 1H), 6.84 (dd, J = 8.8, 2.4 Hz, 1H), 5.94 (s, 1H), 3.81 (s, 3H), 1.93 (s, 3H), 1.66 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 169.2, 153.6, 145.1, 136.7, 132.2, 128.6, 128.1, 126.7, 126.2, 124.91, 124.86, 120.2, 112.1, 111.9, 103.0, 56.0, 35.9, 28.9, 20.7.

HRMS (ESI): Calcd for $C_{22}H_{23}NO_3Na$ $[M+Na]^+$: 372.1570; found: 372.1572.



(*Z*)-3-Methyl-1-phenyl-3-[5-(trifluoromethoxy)-1*H*-indol-3-yl]but-1-en-1-yl acetate (3j)

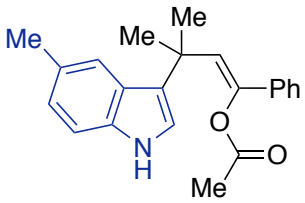
The product was isolated by flash chromatography (ethyl acetate/hexanes 1:10) as yellow oil. 29 mg, 72% yield.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.07 (s, 1H), 7.67 (s, 1H), 7.37-7.36 (m, 2H), 7.31-7.29 (m, 3H), 7.27-7.25 (m, 1H), 7.07 (d, J = 2.4 Hz, 1H), 7.06 (d, J = 8.8 Hz, 1H), 5.93 (s, 1H), 1.86 (s, 3H), 1.66 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 169.0, 145.6, 142.6 (q, J_{CF} = 2.1 Hz), 136.5, 135.4, 128.6, 128.3, 126.5, 125.7, 125.5, 124.9, 121.6, 121.0 (q, J_{CF} = 255.2 Hz), 115.9, 113.7, 111.8, 35.7, 29.2, 20.5.

^{19}F NMR (564.9 MHz, $CDCl_3$): δ -58.0.

HRMS (ESI): Calcd for $C_{22}H_{20}F_3NO_3Na$ $[M+Na]^+$: 426.1287; found: 426.1291.



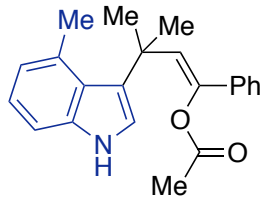
(*Z*)-3-Methyl-3-(5-methyl-1*H*-indol-3-yl)-1-phenylbut-1-en-1-yl acetate (3k)

The product was isolated by flash chromatography (ethyl acetate/hexanes 1:10) as yellow oil. 27 mg, 81% yield in CF_3CH_2OH. When HFIP was used as solvent, **3k** was obtained in 61% yield.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.85 (s, 1H), 7.58 (s, 1H), 7.39 (d, J = 7.6 Hz, 2H), 7.31 (t, J = 7.5 Hz, 2H), 7.27-7.23 (m, 2H), 7.02 (d, J = 8.2 Hz, 1H), 6.96 (d, J = 2.3 Hz, 1H), 6.04 (s, 1H), 2.45 (s, 3H), 1.91 (s, 3H), 1.69 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 169.2, 145.2, 136.6, 135.5, 128.5, 128.3, 128.1, 126.5, 126.4, 124.9, 124.6, 123.5, 120.8, 119.8, 110.9, 35.9, 29.2, 21.8, 20.6.

HRMS (ESI): Calcd for $C_{22}H_{23}NO_2Na$ $[M+Na]^+$: 356.1621; found: 356.1622.



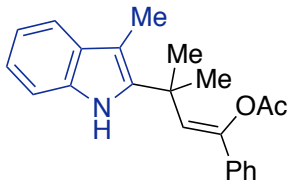
(*Z*)-3-Methyl-3-(4-methyl-1*H*-indol-3-yl)-1-phenylbut-1-en-1-yl acetate (3l)

The product was isolated by flash chromatography (ethyl acetate/hexanes 1:10) as yellow oil. 27 mg, 81% yield in CF_3CH_2OH.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.98 (s, 1H), 7.36 (d, *J* = 7.3 Hz, 2H), 7.31 (t, *J* = 7.6 Hz, 2H), 7.27-7.24 (m, 1H), 7.18 (d, *J* = 8.0 Hz, 1H), 7.10-7.07 (m, 2H), 6.90 (d, *J* = 7.2 Hz, 1H), 6.12 (s, 1H), 2.76 (s, 3H), 1.69 (s, 6H), 1.55 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 168.9, 144.9, 138.2, 136.4, 131.1, 128.6, 128.2, 128.0, 125.9, 125.2, 124.6, 122.2, 122.0, 120.4, 108.9, 35.7, 31.6, 23.1, 19.9.

HRMS (ESI): Calcd for $C_{22}H_{23}NO_2Na$ $[M+Na]^+$: 356.1621; found: 356.1622.



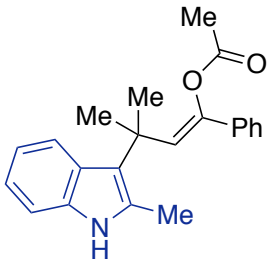
(*Z*)-3-Methyl-3-(3-methyl-1*H*-indol-2-yl)-1-phenylbut-1-en-1-yl acetate (3m)

The product was isolated by flash chromatography (ethyl acetate/hexanes 1:20) as yellow oil. 24 mg, 73% yield in CF_3CH_2OH.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.10 (br s, NH), 7.51 (d, *J* = 7.8 Hz, 1H), 7.40-7.38 (m, 2H), 7.35-7.32 (m, 2H), 7.30-7.28 (m, 2H), 7.14-7.08 (m, 2H), 5.94 (s, 1H), 2.36 (s, 3H), 1.68 (s, 6H), 1.60 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 168.9, 146.4, 139.3, 136.0, 134.3, 130.4, 128.7, 128.4, 125.0, 124.8, 121.2, 119.1, 118.1, 110.4, 106.3, 36.9, 28.9, 20.1, 10.1.

HRMS (ESI): Calcd for $C_{22}H_{23}NO_2Na$ $[M+Na]^+$: 356.1621; found: 356.1623.



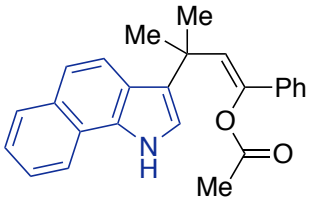
(*Z*)-3-Methyl-3-(2-methyl-1*H*-indol-3-yl)-1-phenylbut-1-en-1-yl acetate (3n)

The product was isolated by flash chromatography (ethyl acetate/hexanes 1:10) as yellow oil. 26 mg, 79% yield in CF_3CH_2OH.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.88 (d, *J* = 8.0 Hz, 1H), 7.76 (s, 1H), 7.38-7.36 (m, 2H), 7.31 (t, *J* = 7.5 Hz, 2H), 7.27-7.24 (m, 1H), 7.22 (d, *J* = 8.0 Hz, 1H), 7.09-7.02 (m, 2H), 6.13 (s, 1H), 2.46 (s, 3H), 1.78 (s, 6H), 1.45 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 168.7, 145.6, 136.4, 135.1, 131.1, 128.6, 128.5, 128.1, 128.0, 124.6, 120.8, 120.4, 119.1, 117.9, 110.3, 37.0, 30.5, 19.9, 15.0.

HRMS (ESI): Calcd for $C_{22}H_{23}NO_2Na$ $[M+Na]^+$: 356.1621; found: 356.1623.



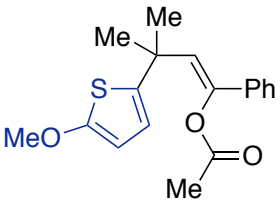
(*Z*)-3-(1*H*-Benzo[*g*]indol-3-yl)-3-methyl-1-phenylbut-1-en-1-yl acetate (3o)

The product was isolated by flash chromatography (ethyl acetate/hexanes 1:20) as yellow oil. 21 mg, 57% yield in CF_3CH_2OH.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.64 (s, 1H), 7.96 (d, J = 8.0 Hz, 1H), 7.88 (t, J = 9.2 Hz, 2H), 7.51-7.45 (m, 2H), 7.42-7.35 (m, 3H), 7.30-7.23 (m, 3H), 7.04 (d, J = 2.5 Hz, 1H), 6.07 (s, 1H), 1.80 (s, 3H), 1.70 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 169.1, 145.4, 136.5, 131.7, 130.3, 128.9, 128.6, 128.2, 127.1, 126.3, 125.4, 124.8, 124.1, 122.4, 121.9, 121.0, 120.1, 119.4, 117.7, 35.9, 29.6, 20.5.

HRMS (ESI): Calcd for $C_{25}H_{23}NO_2Na$ $[M+Na]^+$: 392.1621; found: 392.1624.



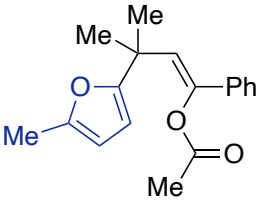
(*Z*)-3-(5-Methoxythiophen-2-yl)-3-methyl-1-phenylbut-1-en-1-yl acetate (3p)

The product was isolated by flash chromatography (ethyl acetate/hexanes 1:25) as yellow oil. 16 mg, 51% yield in CF_3CH_2OH.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38-7.36 (m, 2H), 7.33-7.27 (m, 3H), 6.48 (d, J = 3.9 Hz, 1H), 5.99 (d, J = 3.9 Hz, 1H), 5.82 (s, 1H), 3.85 (s, 3H), 2.08 (s, 3H), 1.56 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 168.9, 164.6, 146.0, 140.7, 136.3, 128.6, 128.3, 125.8, 124.9, 119.4, 102.8, 60.4, 38.4, 30.9, 20.9.

HRMS (ESI): Calcd for $C_{18}H_{20}O_3SNa$ $[M+Na]^+$: 339.1025; found: 339.1029.



(*Z*)-3-(5-Methylfuran-2-yl)-3-methyl-1-phenylbut-1-en-1-yl acetate (3q)

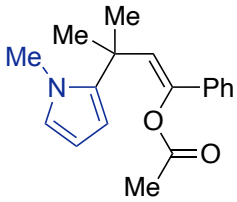
The product was isolated by flash chromatography (ethyl acetate/hexanes 1:50) as yellow oil. 20 mg, 71% yield in HFIP.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 (d, J = 8.7 Hz, 2H), 7.30-7.28 (m, 2H), 7.24 (t, J = 7.2 Hz, 1H), 5.93 (d, J = 3.0 Hz, 1H), 5.84 (d, J = 3.0 Hz, 1H), 5.80 (s, 1H), 2.26 (s, 3H), 1.99 (s, 3H), 1.49 (s, 6H).

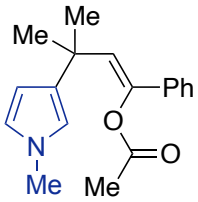
^{13}C NMR (100 MHz, $CDCl_3$): δ 168.8, 159.4, 150.8, 145.7, 136.2, 128.6, 128.2, 124.8, 124.5, 105.7, 103.9, 36.6,

28.2, 20.8, 13.7.

HRMS (ESI): Calcd for $C_{18}H_{20}O_3Na$ $[M+Na]^+$: 307.1305; found: 307.1302.



(major)



(minor)

The product was isolated by flash chromatography (ethyl acetate/hexanes 1:30) as yellow oil. 18 mg, 64% yield in CF_3CH_2OH. The ratio of C2- and C3-isomers was determined to be 2:1 by crude ^1H NMR. The two isomers were separated by silica gel.

(*Z*)-3-Methyl-3-(1-methyl-1H-pyrrol-2-yl)-1-phenylbut-1-en-1-yl acetate (major, 3r)

^1H NMR (600 MHz, $CDCl_3$): δ 7.36 (d, J = 7.1 Hz, 2H), 7.33-7.30 (m, 2H), 7.27 (t, J = 6.8 Hz, 1H), 6.52 (t, J = 2.2 Hz, 1H), 6.01 (t, J = 3.2 Hz, 1H), 5.99 (dd, J = 3.6, 2.0 Hz, 1H), 5.92 (s, 1H), 3.62 (s, 3H), 1.83 (s, 3H), 1.55 (s, 6H).

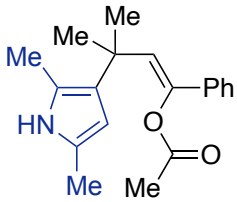
^{13}C NMR (150 MHz, $CDCl_3$): δ 168.9, 146.1, 139.0, 135.9, 128.7, 128.3, 124.9, 124.6, 123.3, 106.2, 104.8, 35.9, 35.4, 29.7, 20.5.

(*Z*)-3-Methyl-3-(1-methyl-1H-pyrrol-3-yl)-1-phenylbut-1-en-1-yl acetate (minor, 3r′)

^1H NMR (600 MHz, $CDCl_3$): δ 7.37 (d, J = 8.2 Hz, 2H), 7.31-7.28 (m, 2H), 7.24 (t, J = 7.2 Hz, 1H), 6.52 (t, J = 2.5 Hz, 1H), 6.46 (t, J = 2.1 Hz, 1H), 6.10 (t, J = 2.3 Hz, 1H), 5.86 (s, 1H), 3.61 (s, 3H), 2.06 (s, 3H), 1.49 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 169.2, 144.5, 136.7, 133.4, 128.5, 128.0, 127.4, 124.7, 121.5, 118.0, 106.8, 36.2, 35.5, 30.3, 20.8.

HRMS (ESI): Calcd for $C_{18}H_{21}NO_2Na$ $[M+Na]^+$: 306.1464; found: 306.1466.



(*Z*)-3-(2,5-Dimethylpyrrol-3-yl)-3-methyl-1-phenylbut-1-en-1-yl acetate (3s)

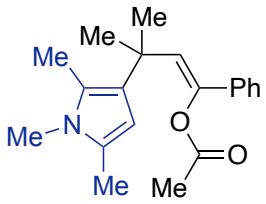
The product was isolated by flash chromatography (ethyl acetate/hexanes 1:20) as yellow oil. 21 mg, 71% yield in CF_3CH_2OH.

^1H NMR (600 MHz, $CDCl_3$): δ 7.40 (s, NH), 7.35 (d, J = 8.7 Hz, 2H), 7.30-7.27 (m, 2H), 7.22 (t, J = 7.3 Hz, 1H), 5.91 (s, 1H), 5.78 (s, 1H), 2.20 (s, 3H), 2.18 (s, 3H), 1.94 (s, 3H), 1.47 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 168.8, 144.9, 136.6, 128.6, 127.9, 127.6, 126.8, 124.5, 123.3, 122.0, 105.0, 34.9,

29.9, 20.6, 13.2, 13.0.

HRMS (ESI): Calcd for $C_{19}H_{23}NO_2Na$ $[M+Na]^+$: 320.1621; found: 320.1621.



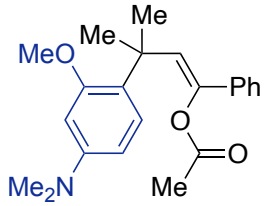
(*Z*)-3-Methyl-1-phenyl-3-(1,2,5-trimethylpyrrol-3-yl)-but-1-en-1-yl acetate (3t)

The product was isolated by flash chromatography (ethyl acetate/hexanes 1:20) as yellow oil. 19 mg, 61% yield in CF_3CH_2OH.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.36 (d, J = 8.6 Hz, 2H), 7.30-7.28 (m, 2H), 7.23 (t, J = 7.3 Hz, 1H), 5.92 (s, 1H), 5.81 (s, 1H), 3.32 (s, 3H), 2.20 (s, 3H), 2.17 (s, 3H), 1.94 (s, 3H), 1.48 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 168.8, 144.7, 136.7, 128.5, 127.9, 127.8, 126.2, 125.1, 124.5, 124.0, 103.6, 35.0, 29.9, 20.6, 12.5, 12.0.

HRMS (ESI): Calcd for $C_{20}H_{25}NO_2Na$ $[M+Na]^+$: 334.1777; found: 334.1778.



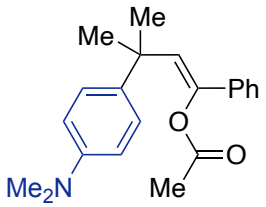
(*Z*)-3-[4-(Dimethylamino)-2-methoxyphenyl]-3-methyl-1-phenylbut-1-en-1-yl acetate (3u)

The product was isolated by flash chromatography (ethyl acetate/hexanes 1:10) as yellow oil. 25 mg, 71% yield in CF_3CH_2OH.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.34 (d, J = 8.6 Hz, 2H), 7.30-7.27 (m, 2H), 7.22 (t, J = 7.3 Hz, 1H), 7.19 (d, J = 8.3 Hz, 1H), 6.31-6.29 (m, 2H), 6.01 (s, 1H), 3.80 (s, 3H), 2.93 (s, 6H), 1.72 (s, 3H), 1.53 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 168.7, 158.8, 150.8, 143.7, 136.9, 128.4, 127.5, 126.3, 125.4, 124.4, 104.5, 98.2, 55.5, 41.1, 37.2, 29.0, 20.4.

HRMS (ESI): Calcd for $C_{22}H_{27}NO_3Na$ $[M+Na]^+$: 376.1883; found: 376.1885.



(Z)-3-[4-(Dimethylamino)phenyl]-3-methyl-1-phenylbut-1-en-1-yl acetate (3v)

The product was isolated by flash chromatography (ethyl acetate/hexanes 1:20) as yellow oil. 21 mg, 65% yield in HFIP.

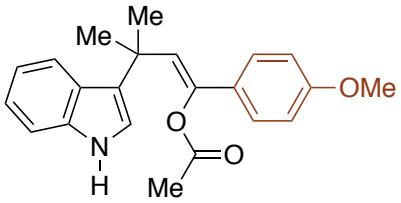
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.36 (d, J = 8.6 Hz, 2H), 7.31-7.27 (m, 4H), 7.25-7.23 (m, 1H), 6.72 (d, J = 9.0 Hz, 2H), 5.88 (s, 1H), 2.92 (s, 6H), 1.89 (s, 3H), 1.52 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 169.0, 149.0, 145.3, 137.3, 136.6, 128.5, 128.0, 127.4, 126.8, 124.7, 112.8, 41.0, 39.2, 30.1, 20.7.

HRMS (ESI): Calcd for $C_{21}H_{26}NO_2$ $[M+H]^+$: 324.1958; found: 324.1955.

(B) The procedure for reactions in the scope of substituted propargylic acetates: Unless otherwise stated, the procedure was as follows. In an argon-filled glove box, $Pd(acac)_2$ (24.5 mg, 0.08 mmol), P(2-furyl)$_3$ (22.3 mg, 0.096 mmol) and 2 mL of trifluoroethanol were charged into an oven-dried 8-mL vial. After stirring for about 30 minutes at rt, the yellow solution of Pd complex was ready for use.

To another oven-dried 4-mL vial, 0.1 mL of the Pd complex (0.004 mmol, 4 mol%) from the stock solution was added under argon, followed by the sequential addition of 1*H*-indole (17.6 mg, 0.15 mmol), formic acid (0.8 μL, 0.02 mmol) and substituted propargylic acetate (0.1 mmol). The vial was sealed with a screw cap and placed in a heating block maintained at 30 °C. After stirring for 24 hours, the crude reaction mixture was purified by flash chromatography on silica using ethyl acetate/hexanes as eluent.



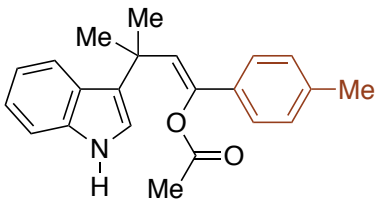
(*Z*)-3-(1*H*-Indol-3-yl)-1-(4-methoxyphenyl)-3-methylbut-1-en-1-yl acetate (4a)

The product was isolated by flash chromatography (ethyl acetate/hexanes 1:5) as white solid. 31 mg, 89% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (s, 1H), 7.80 (d, J = 7.9 Hz, 1H), 7.35-7.33 (m, 1H), 7.30 (d, J = 9.1 Hz, 2H), 7.18 (t, J = 7.5 Hz, 1H), 7.09 (t, J = 7.4 Hz, 1H), 6.99 (d, J = 2.4 Hz, 1H), 6.82 (d, J = 9.1 Hz, 2H), 5.92 (s, 1H), 3.78 (s, 3H), 1.88 (s, 3H), 1.67 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 169.2, 159.6, 145.0, 137.1, 129.2, 126.3, 126.2, 125.3, 124.6, 121.8, 121.2, 119.5, 119.2, 114.0, 111.3, 55.4, 35.7, 29.3, 20.6.

HRMS (ESI): Calcd for $C_{22}H_{23}NO_3Na$ $[M+Na]^+$: 372.1570; found: 372.1573.



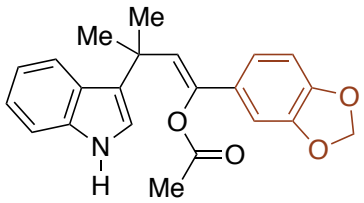
(*Z*)-3-(1*H*-Indol-3-yl)-3-methyl-1-(*p*-tolyl)-but-1-en-1-yl acetate (4b)

The product was isolated by flash chromatography (ethyl acetate/hexanes 1:10) as brown oil. 27 mg, 81% yield.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.93 (s, 1H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.35 (d, *J* = 8.2 Hz, 1H), 7.26 (d, *J* = 8.2 Hz, 2H), 7.18 (t, *J* = 7.6 Hz, 1H), 7.10-7.07 (m, 3H), 7.00 (d, *J* = 2.3 Hz, 1H), 5.99 (s, 1H), 2.32 (s, 3H), 1.88 (s, 3H), 1.67 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 169.2, 145.4, 138.0, 137.1, 133.7, 129.2, 126.3, 125.4, 125.3, 124.7, 121.9, 121.2, 119.5, 119.3, 111.2, 35.8, 29.2, 21.2, 20.6.

HRMS (ESI): Calcd for $C_{22}H_{23}NO_2Na$ $[M+Na]^+$: 356.1626; found: 356.1611.



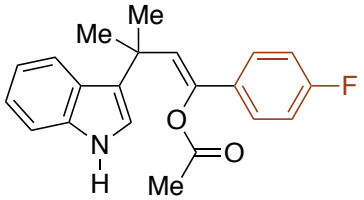
(Z)-1-(Benzo[d][1,3]dioxol-5-yl)-3-(1H-indol-3-yl)-3-methylbut-1-en-1-yl acetate (4c)

The product was isolated by flash chromatography (ethyl acetate/hexanes 1:5) as brown oil. 29 mg, 80% yield.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.95 (s, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.34 (d, *J* = 8.1 Hz, 1H), 7.18 (t, *J* = 7.5 Hz, 1H), 7.09 (t, *J* = 7.5 Hz, 1H), 6.99 (d, *J* = 2.3 Hz, 1H), 6.87-6.85 (m, 2H), 6.72 (d, *J* = 8.6 Hz, 1H), 5.92 (s, 2H), 5.89 (s, 1H), 1.87 (s, 3H), 1.66 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 169.1, 147.9, 147.6, 144.9, 137.1, 131.0, 126.3, 125.2, 121.9, 121.1, 119.5, 119.3, 118.8, 111.3, 108.3, 105.6, 101.3, 35.8, 29.2, 20.6.

HRMS (ESI): Calcd for $C_{22}H_{21}NO_4Na$ $[M+Na]^+$: 386.1363; found: 386.1367.



(Z)-1-(4-Fluorophenyl)-3-(1H-indol-3-yl)-3-methylbut-1-en-1-yl acetate (4d)

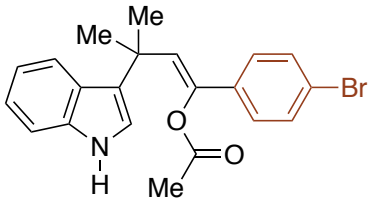
The product was isolated by flash chromatography (ethyl acetate/hexanes 1:5) as yellow oil. 27 mg, 81% yield.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.95 (s, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.36-7.32 (m, 3H), 7.19 (t, *J* = 7.6 Hz, 1H), 7.10 (t, *J* = 7.5 Hz, 1H), 7.00-6.96 (m, 3H), 5.95 (s, 1H), 1.88 (s, 3H), 1.67 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 169.1, 162.6 (d, J_{CF} = 247.4 Hz), 144.4, 137.1, 132.8 (d, J_{CF} = 3.3 Hz), 126.7 (d, J_{CF} = 8.3 Hz), 126.3, 126.2 (d, J_{CF} = 1.6 Hz), 125.1, 122.0, 121.1, 119.5, 119.3, 115.5 (d, J_{CF} = 21.7 Hz), 111.3, 35.8, 29.2, 20.6.

^{19}F NMR (564.9 MHz, $CDCl_3$): δ -113.9.

HRMS (ESI): Calcd for $C_{21}H_{20}FNO_2Na$ $[M+Na]^+$: 360.1370; found: 360.1374.



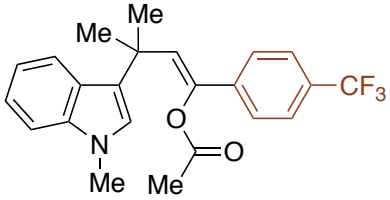
(Z)-1-(4-Bromophenyl)-3-(1H-indol-3-yl)-3-methylbut-1-en-1-yl acetate (4e)

The product was isolated by flash chromatography (ethyl acetate/hexanes 1:5) as yellow oil. 33 mg, 83% yield.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.95 (s, 1H), 7.76 (d, J = 8.0 Hz, 1H), 7.41 (d, J = 8.4 Hz, 2H), 7.35 (d, J = 8.1 Hz, 1H), 7.23 (d, J = 8.4 Hz, 2H), 7.19 (t, J = 7.5 Hz, 1H), 7.09 (t, J = 7.5 Hz, 1H), 7.00 (d, J = 2.4 Hz, 1H), 6.01 (s, 1H), 1.88 (s, 3H), 1.67 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 169.0, 144.4, 137.1, 135.6, 131.7, 127.0, 126.5, 126.2, 125.0, 122.05, 121.98, 121.0, 119.5, 119.4, 111.3, 35.9, 29.1, 20.5.

HRMS (ESI): Calcd for $C_{21}H_{20}{}^{79}BrNO_2Na$ $[M+Na]^+$: 420.0570; found: 420.0569.



(Z)-3-Methyl-3-(1-methyl-1H-indol-3-yl)-1-(4-(trifluoromethyl)phenyl)but-1-en-1-yl acetate (4f)

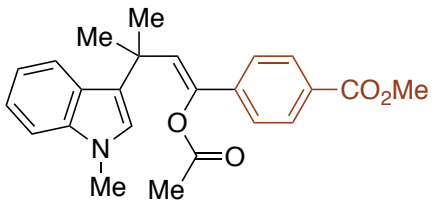
The product was isolated by flash chromatography (ethyl acetate/hexanes 1:40) as yellow oil. 28 mg, 70% yield in HFIP.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.74 (d, J = 8.0 Hz, 1H), 7.54 (d, J = 8.4 Hz, 2H), 7.46 (d, J = 8.4 Hz, 2H), 7.31 (d, J = 8.2 Hz, 1H), 7.23 (t, J = 7.6 Hz, 1H), 7.09 (t, J = 7.5 Hz, 1H), 6.88 (s, 1H), 6.10 (s, 1H), 3.77 (s, 3H), 1.91 (s, 3H), 1.68 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 168.9, 144.0, 140.1 (q, J_{CF} = 1.5 Hz), 137.8, 129.9 (q, J_{CF} = 32.5 Hz), 128.8, 126.6, 125.6 (q, J_{CF} = 4.1 Hz), 125.1, 124.5, 123.3, 121.6, 121.0, 118.9, 109.4, 100.0, 36.0, 32.7, 29.1, 20.5.

^{19}F NMR (564.9 MHz, $CDCl_3$): δ -62.5.

HRMS (ESI): Calcd for $C_{23}H_{22}F_3NO_2Na$ $[M+Na]^+$: 424.1495; found: 424.1496.



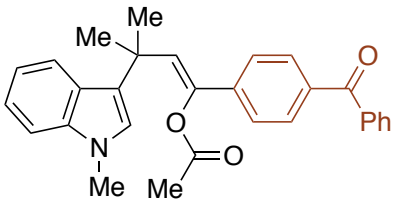
Methyl (Z)-4-(1-acetoxy-3-methyl-3-(1-methyl-1H-indol-3-yl)but-1-en-1-yl)benzoate (4g)

The product was isolated by flash chromatography (ethyl acetate/hexanes 1:30) as yellow oil. 32 mg, 82% yield in HFIP.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.95 (d, *J* = 8.4 Hz, 2H), 7.75 (d, *J* = 7.9 Hz, 1H), 7.41 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8.1 Hz, 1H), 7.22 (t, *J* = 7.6 Hz, 1H), 7.08 (t, *J* = 7.5 Hz, 1H), 6.87 (s, 1H), 6.13 (s, 1H), 3.90 (s, 3H), 3.76 (s, 3H), 1.91 (s, 3H), 1.68 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 168.9, 166.8, 144.3, 140.9, 137.8, 129.9, 129.5, 128.8, 126.6, 124.6, 124.5, 123.3, 121.6, 121.1, 118.9, 109.4, 52.2, 36.1, 32.7, 29.1, 20.5.

HRMS (ESI): Calcd for $C_{24}H_{25}NO_4Na$ $[M+Na]^+$: 414.1676; found: 414.1679.



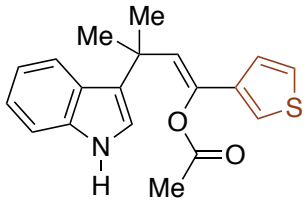
(*Z*)-1-(4-Benzoylphenyl)-3-methyl-3-(1-methyl-1H-indol-3-yl)but-1-en-1-yl acetate (4h)

The product was isolated by flash chromatography (ethyl acetate/hexanes 1:10) as pale-yellow oil. 32 mg, 74% yield in HFIP.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.77-7.75 (m, 3H), 7.73 (d, *J* = 8.4 Hz, 2H), 7.57 (t, *J* = 7.3 Hz, 1H), 7.47 (d, *J* = 7.7 Hz, 2H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8.2 Hz, 1H), 7.22 (t, *J* = 7.6 Hz, 1H), 7.09 (t, *J* = 7.5 Hz, 1H), 6.88 (s, 1H), 6.17 (s, 1H), 3.76 (s, 3H), 1.92 (s, 3H), 1.69 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 196.1, 168.9, 144.3, 140.4, 137.8, 137.7, 136.8, 132.5, 130.5, 130.1, 128.9, 128.4, 126.6, 124.54, 124.48, 123.3, 121.6, 121.1, 118.9, 109.4, 36.1, 32.7, 29.1, 20.5.

HRMS (ESI): Calcd for $C_{29}H_{28}NO_3$ $[M+H]^+$: 438.2064; found: 438.2067.



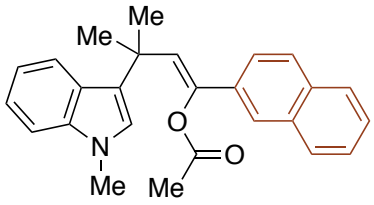
(*Z*)-3-(1*H*-Indol-3-yl)-3-methyl-1-(thiophen-3-yl)but-1-en-1-yl acetate (4i)

The product was isolated by flash chromatography (ethyl acetate/hexanes 1:10) as brown oil. 24 mg, 74% yield.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.96 (s, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.35 (d, *J* = 8.1 Hz, 1H), 7.23 (dd, *J* = 5.1, 3.0 Hz, 1H), 7.18 (t, *J* = 7.6 Hz, 1H), 7.12 (dd, *J* = 5.1, 1.2 Hz, 1H), 7.09 (t, *J* = 7.5 Hz, 1H), 7.05 (dd, *J* = 3.0, 1.2 Hz, 1H), 6.99 (d, *J* = 2.4 Hz, 1H), 5.99 (s, 1H), 1.86 (s, 3H), 1.66 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 169.2, 141.5, 138.3, 137.1, 126.4, 126.2, 125.5, 124.94, 124.92, 121.9, 121.2, 120.3, 119.6, 119.3, 111.3, 35.7, 29.2, 20.5.

HRMS (ESI): Calcd for $C_{19}H_{19}NO_2SNa$ $[M+Na]^+$: 348.1029; found: 348.1031.



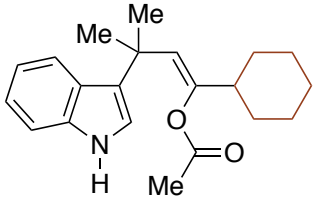
(*Z*)-3-Methyl-3-(1-methyl-1*H*-indol-3-yl)-1-(naphthalen-2-yl)but-1-en-1-yl acetate (4j)

The product was isolated by flash chromatography (ethyl acetate/hexanes 1:20) as yellow oil. 27 mg, 71% yield.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.83 (d, *J* = 8.0 Hz, 1H), 7.79-7.76 (m, 4H), 7.55 (dd, *J* = 8.7, 1.7 Hz, 1H), 7.46-7.43(m, 2H), 7.32 (d, *J* = 8.2 Hz, 1H), 7.24 (t, *J* = 7.6 Hz, 1H), 7.10 (t, *J* = 7.5 Hz, 1H), 6.91 (s, 1H), 6.18 (s, 1H), 3.78 (s, 3H), 1.96 (s, 3H), 1.73 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 169.1, 145.2, 137.8, 133.9, 133.3, 133.1, 128.4, 128.3, 127.7, 127.1, 126.7, 126.4, 126.2, 124.5, 123.7, 123.6, 123.0, 121.5, 121.3, 118.8, 109.3, 36.0, 32.7, 29.3, 20.6.

HRMS (ESI): Calcd for $C_{26}H_{25}NO_2Na$ $[M+Na]^+$: 406.1777; found: 406.1782.



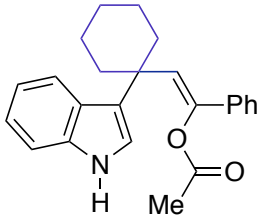
(Z)-1-Cyclohexyl-3-(1H-indol-3-yl)-3-methylbut-1-en-1-yl acetate (4k)

The product was isolated by flash chromatography (ethyl acetate/hexanes 1:10) as brown oil. 22 mg, 68% yield.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.88 (s, 1H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.34 (d, *J* = 8.1 Hz, 1H), 7.17 (t, *J* = 7.6 Hz, 1H), 7.08 (t, *J* = 7.5 Hz, 1H), 6.94 (d, *J* = 2.4 Hz, 1H), 5.21 (s, 1H), 2.09-2.05 (m, 1H), 1.88-1.86 (m, 2H), 1.73 (s, 3H), 1.74-1.71 (m, 2H), 1.64-1.62 (m, 2H), 1.53 (s, 6H), 1.23-1.18 (m, 2H), 1.14-1.09 (m, 2H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 169.4, 151.7, 137.1, 126.4, 125.6, 121.8, 121.7, 121.4, 119.3, 118.9, 111.2, 42.5, 35.0, 31.4, 29.4, 26.3, 20.6.

HRMS (ESI): Calcd for $C_{21}H_{27}NO_2Na$ $[M+Na]^+$: 348.1934; found: 348.1938.



(*Z*)-2-[1-(1*H*-Indol-3-yl)cyclohexyl]-1-phenylvinyl acetate (4l)

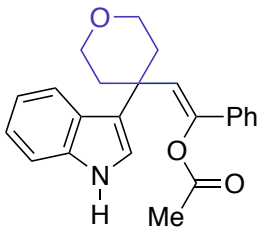
The product was isolated by flash chromatography (ethyl acetate/hexanes 1:10) as yellow oil. 27 mg, 76% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (s, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.37 (d, *J* = 7.4 Hz, 2H), 7.33-7.28 (m, 3H), 7.25-7.22 (m, 1H), 7.14 (t, *J* = 7.3 Hz, 1H), 7.05-7.03 (m, 2H), 6.07 (s, 1H), 2.29-2.26 (m, 2H), 2.05-2.01 (m, 2H), 1.72 (s, 3H), 1.68-1.65 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 168.6, 146.5, 137.1, 136.8, 128.6, 128.0, 126.2, 124.8, 124.7, 123.8, 121.6, 121.5,

120.6, 119.0, 111.3, 39.8, 37.6, 26.4, 23.1, 20.4.

HRMS (ESI): Calcd for $C_{24}H_{25}NO_2Na$ $[M+Na]^+$: 382.1783; found: 382.1778.



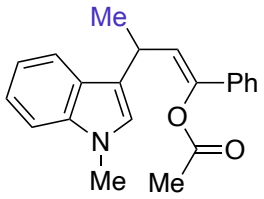
(*Z*)-2-[4-(1*H*-Indol-3-yl)tetrahydro-2*H*-pyran-4-yl]-1-phenylvinyl acetate (4m)

The product was isolated by flash chromatography (ethyl acetate/hexanes 1:3) as orange oil. 21 mg, 59% yield in HFIP.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.02 (s, 1H), 7.73 (d, J = 8.1 Hz, 1H), 7.38-7.35 (m, 3H), 7.32-7.26 (m, 3H), 7.17 (t, J = 7.6 Hz, 1H), 7.09-7.06 (m, 2H), 6.09 (s, 1H), 3.91-3.82 (m, 4H), 2.37-2.25 (m, 4H), 1.76 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 168.3, 147.5, 137.2, 136.4, 128.6, 128.4, 125.9, 124.9, 123.2, 122.1, 122.0, 121.1, 120.8, 119.4, 111.5, 64.9, 37.5, 37.4, 20.5.

HRMS (ESI): Calcd for $C_{23}H_{23}NO_3Na$ $[M+Na]^+$: 384.1570; found: 384.1574.



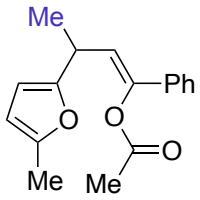
(*Z*)-3-(1-Methyl-1*H*-indol-3-yl)-1-phenylbut-1-en-1-yl acetate (4n)

The product was isolated by flash chromatography (ethyl acetate/hexanes 1:20) as yellow oil. 22 mg, 69% yield in HFIP.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.70 (d, J = 7.9 Hz, 1H), 7.41 (d, J = 7.2 Hz, 2H), 7.31-7.28 (m, 4H), 7.22 (t, J = 7.6 Hz, 1H), 7.10 (t, J = 7.4 Hz, 1H), 6.89 (s, 1H), 5.94 (d, J = 9.8 Hz, 1H), 4.05-4.00 (m, 1H), 3.76 (s, 3H), 2.34 (s, 3H), 1.53 (d, J = 9.9 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 169.2, 144.8, 137.4, 135.2, 128.6, 128.2, 127.3, 125.1, 124.7, 123.4, 121.8, 119.8, 119.0, 118.6, 109.3, 32.8, 28.8, 20.9, 20.5.

HRMS (ESI): Calcd for $C_{21}H_{21}NO_2Na$ $[M+Na]^+$: 342.1464; found: 342.1465.



(*Z*)-3-(5-Methylfuran-2-yl)-1-phenylbut-1-en-1-yl acetate (4o)

The product was isolated by flash chromatography (ethyl acetate/hexanes 1:40) as yellow oil. 17 mg, 63% yield in HFIP.

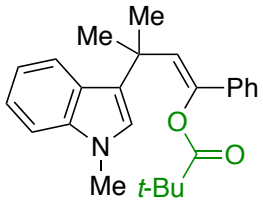
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.42 (d, J = 8.6 Hz, 2H), 7.34-7.31 (m, 2H), 7.28 (t, J = 7.3 Hz, 1H), 5.92 (d, J = 3.0 Hz, 1H), 5.86-5.84 (m, 2H), 3.82-3.76 (m, 1H), 2.30 (s, 3H), 2.25 (s, 3H), 1.39 (d, J = 7.0 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 169.0, 155.9, 151.0, 146.1, 135.0, 128.6, 128.5, 124.7, 120.2, 106.0, 104.9, 31.1, 20.8, 19.2, 13.7.

HRMS (ESI): Calcd for $C_{17}H_{18}O_3Na$ $[M+Na]^+$: 293.1148; found: 293.1139.

(C) The procedure for reactions in the scope of propargylic esters: Unless otherwise stated, the procedure was as follows. In an argon-filled glove box, $Pd(acac)_2$ (24.5 mg, 0.08 mmol), P(2-furyl)$_3$ (22.3 mg, 0.096 mmol) and 2 mL of HFIP were charged into an oven-dried 8-mL vial. After stirring for about 30 minutes at rt, the yellow solution of Pd complex was ready for use.

To another oven-dried 4-mL vial, 0.1 mL of the Pd complex (0.004 mmol, 4 mol%) from the stock solution was added under argon, followed by the sequential addition of *N*-methyl indole (19 μL, 0.15 mmol), formic acid (0.8 μL, 0.02 mmol) and propargylic ester (0.1 mmol). The vial was sealed with a screw cap and placed in a heating block maintained at 30 °C. After stirring for 24 hours, the crude reaction mixture was purified by flash chromatography on silica using ethyl acetate/hexanes as eluent.



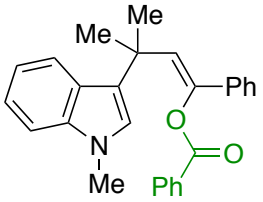
(*Z*)-3-Methyl-3-(1-methyl-1*H*-indol-3-yl)-1-phenylbut-1-en-1-yl pivalate (5a)

The product was isolated by flash chromatography (ethyl acetate/hexanes 1:40) as pale-yellow oil. 29 mg, 78% yield.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.84 (d, J = 8.0 Hz, 1H), 7.39-7.37 (m, 2H), 7.31-7.28 (m, 3H), 7.27-7.22 (m, 2H), 7.11 (t, J = 7.0 Hz, 1H), 6.88 (s, 1H), 5.98 (s, 1H), 3.75 (s, 3H), 1.69 (s, 6H), 1.20 (s, 9H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 176.2, 145.9, 137.8, 137.6, 128.4, 128.0, 127.2, 126.5, 125.1, 124.5, 124.1, 121.4, 121.2, 118.7, 109.3, 39.0, 35.8, 32.7, 29.3, 27.2.

HRMS (ESI): Calcd for $C_{25}H_{29}NO_2Na$ $[M+Na]^+$: 398.2090; found: 398.2094.



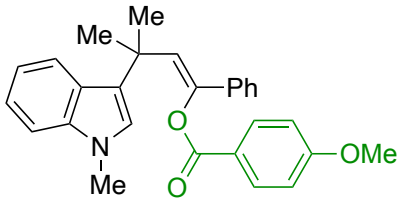
(*Z*)-3-Methyl-3-(1-methyl-1*H*-indol-3-yl)-1-phenylbut-1-en-1-yl benzoate (5b)

The product was isolated by flash chromatography (ethyl acetate/hexanes 1:30) as white solid. 30 mg, 76% yield.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.80 (d, J = 8.0 Hz, 1H), 7.57 (d, J = 6.9 Hz, 2H), 7.54 (t, J = 7.3 Hz, 1H), 7.42 (d, J = 7.8 Hz, 2H), 7.34-7.31 (m, 2H), 7.30-7.27 (m, 2H), 7.25-7.23 (m, 2H), 7.18 (d, J = 8.0 Hz, 1H), 7.11 (t, J = 7.0 Hz, 1H), 6.68 (s, 1H), 6.20 (s, 1H), 3.33 (s, 3H), 1.68 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 164.2, 145.0, 137.8, 136.3, 133.1, 129.9, 129.3, 128.5, 128.2, 128.1, 126.9, 126.3, 124.8, 124.5, 122.9, 121.3, 121.2, 118.6, 109.3, 35.7, 32.1, 29.7.

HRMS (ESI): Calcd for $C_{27}H_{25}NO_2Na$ $[M+Na]^+$: 418.1777; found: 418.1781.



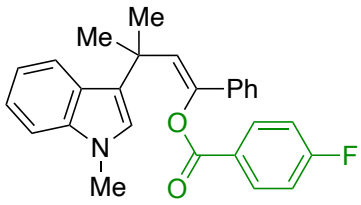
(*Z*)-3-Methyl-3-(1-methyl-1*H*-indol-3-yl)-1-phenylbut-1-en-1-yl 4-methoxybenzoate (5c)

The product was isolated by flash chromatography (ethyl acetate/hexanes 1:20) as yellow oil. 30 mg, 70% yield.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.80 (d, J = 8.1 Hz, 1H), 7.55 (d, J = 8.8 Hz, 2H), 7.40 (d, J = 7.6 Hz, 2H), 7.28-7.19 (m, 5H), 7.10 (t, J = 7.3 Hz, 1H), 6.82 (d, J = 8.8 Hz, 2H), 6.70 (s, 1H), 6.17 (s, 1H), 3.86 (s, 3H), 3.41(s, 3H), 1.67 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 164.1, 163.5, 145.0, 137.7, 136.5, 132.1, 128.5, 128.0, 126.8, 126.3, 124.8, 124.5, 123.2, 121.7, 121.3, 121.2, 118.6, 113.5, 109.3, 55.6, 35.7, 32.3, 29.6.

HRMS (ESI): Calcd for $C_{28}H_{27}NO_3Na$ $[M+Na]^+$: 448.1883; found: 448.1890.



(*Z*)-3-Methyl-3-(1-methyl-1H-indol-3-yl)-1-phenylbut-1-en-1-yl 4-fluorobenzoate (5d)

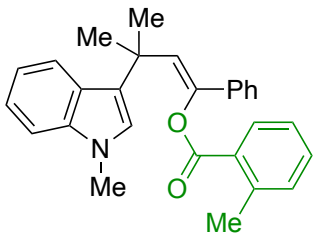
The product was isolated by flash chromatography (ethyl acetate/hexanes 1:40) as yellow oil. 38 mg, 93% yield.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.79 (d, J = 8.0 Hz, 1H), 7.49 (dd, J = 8.9, 5.5 Hz, 2H), 7.41 (d, J = 6.9 Hz, 2H), 7.31-7.23 (m, 4H), 7.18 (d, J = 8.3 Hz, 1H), 7.11 (t, J = 7.4 Hz, 1H), 6.99 (t, J = 8.7 Hz, 2H), 6.67 (s, 1H), 6.19 (s, 1H), 3.36 (s, 3H), 1.67 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 165.8 (d, J_{CF} = 254.3 Hz), 163.2, 144.7, 137.7, 136.1, 132.5 (d, J_{CF} = 9.4 Hz), 128.6, 128.2, 126.9, 126.3, 125.4 (d, J_{CF} = 2.9 Hz), 124.8, 124.5, 122.7, 121.4, 121.2, 118.6, 115.2 (d, J_{CF} = 21.9 Hz), 109.3, 35.6, 32.1, 29.8.

^{19}F NMR (564.9 MHz, $CDCl_3$): δ -105.3.

HRMS (ESI): Calcd for $C_{27}H_{24}FNO_2Na$ $[M+Na]^+$: 436.1683; found: 436.1686.



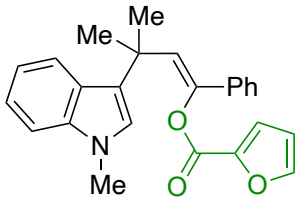
(*Z*)-3-Methyl-3-(1-methyl-1*H*-indol-3-yl)-1-phenylbut-1-en-1-yl 2-methylbenzoate (5e)

The product was isolated by flash chromatography (ethyl acetate/hexanes 1:40) as yellow oil. 27 mg, 66% yield.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.79 (d, *J* = 8.0 Hz, 1H), 7.52 (d, *J* = 7.8 Hz, 1H), 7.43 (d, *J* = 7.1 Hz, 2H), 7.40 (t, *J* = 7.5 Hz, 1H), 7.30-7.24 (m, 3H), 7.20-7.14 (m, 4H), 7.09 (t, *J* = 8.0 Hz, 1H), 6.68 (s, 1H), 6.18 (s, 1H), 3.38 (s, 3H), 2.40 (s, 3H), 1.68 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 164.3, 145.4, 141.8, 137.7, 136.6, 132.4, 131.8, 131.3, 128.6, 128.0, 127.8, 126.7, 126.5, 125.6, 124.8, 124.4, 123.2, 121.4, 121.3, 118.6, 109.2, 35.6, 32.2, 29.7, 22.1.

HRMS (ESI): Calcd for $C_{28}H_{27}NO_2Na$ $[M+Na]^+$: 432.1934; found: 432.1939.



(*Z*)-3-Methyl-3-(1-methyl-1*H*-indol-3-yl)-1-phenylbut-1-en-1-yl furan-2-carboxylate (5f)

The product was isolated by flash chromatography (ethyl acetate/hexanes 1:20) as yellow oil. 18 mg, 47% yield.

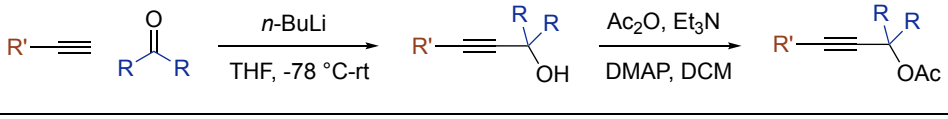
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.77 (d, *J* = 7.9 Hz, 1H), 7.55 (s, 1H), 7.39 (d, *J* = 7.0 Hz, 2H), 7.29-7.24 (m, 3H), 7.21 (d, *J* = 3.6 Hz, 2H), 7.09-7.06 (m, 1H), 6.75 (s, 1H), 6.49 (d, *J* = 3.5 Hz, 1H), 6.43 (dd, *J* = 3.5, 1.8 Hz, 1H), 6.15 (s, 1H), 3.52 (s, 3H), 1.67 (s, 6H).

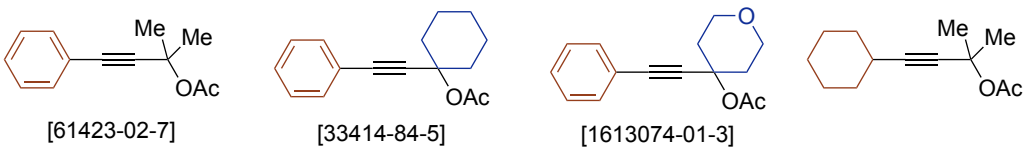
^{13}C NMR (150 MHz, $CDCl_3$): δ 156.4, 146.9, 144.0, 143.9, 137.8, 136.0, 128.6, 128.2, 126.8, 126.7, 124.9, 124.6, 122.8, 121.4, 121.2, 118.6, 118.5, 111.8, 109.2, 35.8, 32.4, 29.5.

HRMS (ESI): Calcd for $C_{25}H_{23}NO_3Na$ $[M+Na]^+$: 408.1570; found: 408.1576.

IV. Substrate synthesis

Table S5. The scope of substituted propargylic acetates[1,2]



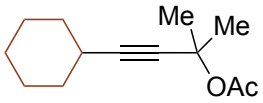


[61423-02-7] [33414-84-5] [1613074-01-3]

Method A: Under argon, a solution of 2M *n*-BuLi in cyclohexane (2.5 mL, 5 mmol) was added to a solution of

terminal alkyne (5 mmol) in anhydrous THF (10 mL) at -78 ºC. After the reaction was stirred for another 15 minutes, dialkyl ketone (5.5 mmol) in anhydrous THF (5 mL) was added dropwise. After the addition, the mixture was warmed to rt and quenched with aqueous NH_4Cl (5 mL) and extracted with ethyl acetate. The combined organic layers were dried over Na_2SO_4, concentrated and used directly in the next step without purification.

To a solution of the crude alcohol in dry DCM (10 mL) was added Et_3N (1 mL, 7.2 mmol), Ac_2O (0.7 mL, 7.4 mmol) and DMAP (50 mg) at rt. After stirring at rt overnight, the reaction mixture was concentrated directly under vacuum and subjected to flash chromatography using ethyl acetate/hexanes as elute.

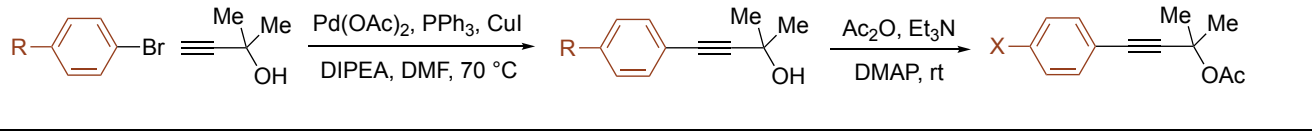


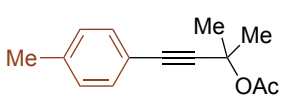
4-Cyclohexyl-2-methylbut-3-yn-2-yl acetate

^{1}H NMR (600 MHz, $CDCl_3$): δ 2.39-2.35 (m, 1H), 1.98 (s, 3H), 1.74-1.71 (m, 2H), 1.68-1.64 (m, 2H), 1.61 (s, 6H), 1.48-1.38 (m, 3H), 1.31-1.23 (m, 3H).

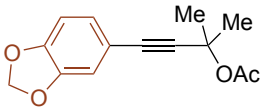
^{13}C NMR (150 MHz, $CDCl_3$): δ 169.5, 88.7, 81.6, 72.8, 32.6, 29.5, 28.9, 26.0, 24.8, 22.3.

LC-MS (ESI): Calcd for $C_{13}H_{21}O_2$ $[M+H]^+$: 209.15; found: 209.15.

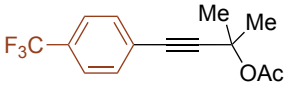




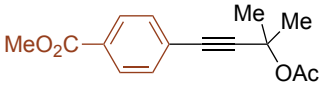
[1402591-93-8]



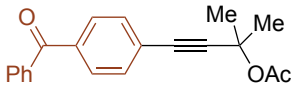
[2143129-64-8]



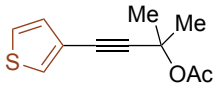
[1402592-02-2]



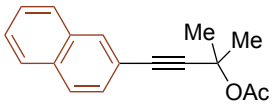
[2375047-24-6]



[2143129-67-1]



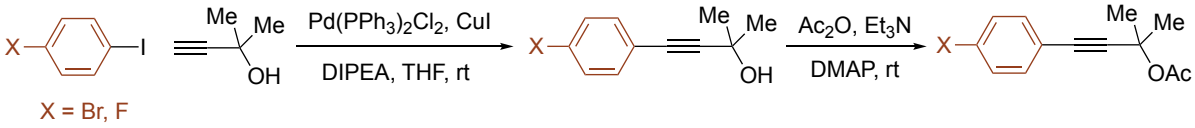
[2143129-66-0]



[2143129-58-0]

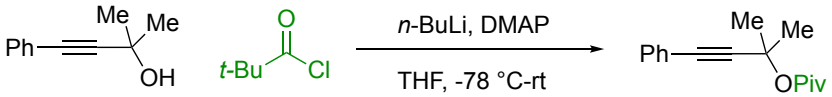
Method B: Under argon, $Pd(OAc)_2$ (56 mg, 0.25 mmol), CuI (95.2 mg, 0.5 mmol), PPh_3 (131.1 mg, 0.5 mmol) and anhydrous DMF (10 mL) were added to a dry flask and the mixture was stirred at room temperature for 10 minutes. Afterwards, aryl bromide (5 mmol), 2-methylbut-3-yn-2-ol (727 µL, 7.5 mmol) and DIPEA (3.5 mL, 20 mmol) were added successively at room temperature, then the resulting mixture was heated at 70 ºC overnight. The reaction was quenched with saturated NH_4Cl solution and extracted with diethyl ether. The organic layers were combined, dried with Na_2SO_4 and concentrated under the reduced pressure. The crude product was directly used in the next step.

To a solution of the crude alcohol in DCM (10 mL) was added Et_3N (1 mL, 7.2 mmol), Ac_2O (0.7 mL, 7.4 mmol) and DMAP (50 mg) at rt. After stirring at rt overnight, the reaction mixture was concentrated directly under vacuum and subjected to flash chromatography using ethyl acetate/hexanes as elute.



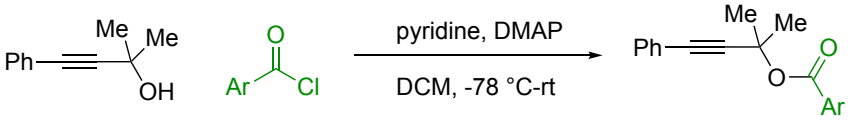
Method C: Under argon, $Pd(PPh_3)_2Cl_2$ (140.4 mg, 0.2 mmol), CuI (38.1 mg, 0.2 mmol) and anhydrous THF (10 mL) were added to a dry flask and the mixture was stirred at room temperature for 5 minutes. Afterwards, aryl iodide (5 mmol), 2-methylbut-3-yn-2-ol (504 µL, 5.2 mmol) and DIPEA (1.5 mL, 8.5 mmol) were added successively at rt. After stirring overnight, the reaction was quenched with saturated NH_4Cl solution and extracted with ethyl acetate. The organic layers were combined, dried with Na_2SO_4 and concentrated under the reduced pressure. The crude product was directly used in the next step.

To a solution of the crude alcohol in DCM (10 mL) was added Et_3N (1 mL, 7.2 mmol), Ac_2O (0.7 mL, 7.4 mmol) and DMAP (50 mg) at rt. After stirring at rt overnight, the reaction mixture was concentrated directly under vacuum and subjected to flash chromatography using ethyl acetate/hexanes as elute.



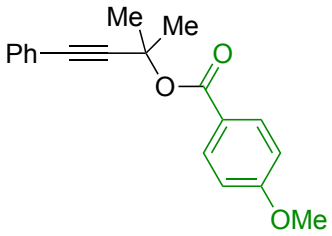
2-Methyl-4-phenylbut-3-yn-2-yl pivalate [1911590-37-8][3]

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.42-7.39 (m, 2H), 7.28-7.25 (m, 3H), 1.73 (s, 6H), 1.19 (s, 9H).



2-Methyl-4-phenylbut-3-yn-2-yl benzoate [41930-23-8][4]

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.06 (d, J = 7.7 Hz, 2H), 7.55 (t, J = 7.4 Hz, 1H), 7.46-7.43 (m, 4H), 7.29-7.26 (m, 3H), 1.91 (s, 6H).

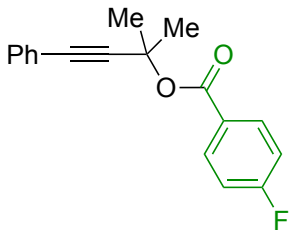


2-Methyl-4-phenylbut-3-yn-2-yl 4-methoxybenzoate

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.99 (d, J = 9.1 Hz, 2H), 7.44-7.42 (m, 2H), 7.27-7.25 (m, 3H), 6.90 (d, J = 9.1 Hz, 2H), 3.85 (s, 3H), 1.88 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 164.7, 163.4, 132.0, 131.8, 128.4, 128.3, 123.7, 122.9, 113.6, 90.6, 84.2, 72.8, 55.6, 29.4.

LC-MS (ESI): Calcd for $C_{19}H_{19}O_3$ $[M+H]^+$: 295.13; found: 295.17.



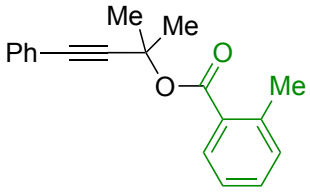
2-Methyl-4-phenylbut-3-yn-2-yl 4-fluorobenzoate

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.05 (dd, *J* = 9.0, 5.5 Hz, 2H), 7.44-7.42 (m, 2H), 7.28-7.26 (m, 3H), 7.11-7.08 (m, 2H), 1.89 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 165.8 (d, *J* = 253.2 Hz), 164.0, 132.3 (d, *J* = 9.2 Hz), 132.0, 128.5, 128.3, 127.5, 122.7, 115.5 (d, *J* = 21.9 Hz), 90.2, 84.5, 73.5, 29.4.

^{19}F NMR (564.9 MHz, $CDCl_3$): δ -106.1.

LC-MS (ESI): Calcd for $C_{18}H_{16}FO_2$ $[M+H]^+$: 283.11; found: 283.23.

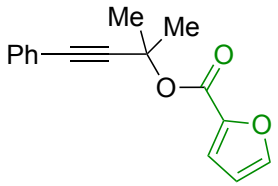


2-Methyl-4-phenylbut-3-yn-2-yl 2-methylbenzoate

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.89 (d, *J* = 7.7 Hz, 1H), 7.46-7.44 (m, 2H), 7.38 (t, *J* = 7.5 Hz, 1H), 7.30-7.28 (m, 3H), 7.25-7.23 (m, 2H), 2.62 (s, 3H), 1.89 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 166.2, 140.0, 132.0, 131.9, 131.8, 130.8, 130.6, 128.4, 128.3, 125.8, 122.8, 90.4, 84.3, 73.2, 29.4, 21.9.

LC-MS (ESI): Calcd for $C_{19}H_{19}O_2$ $[M+H]^+$: 279.14; found: 279.17.



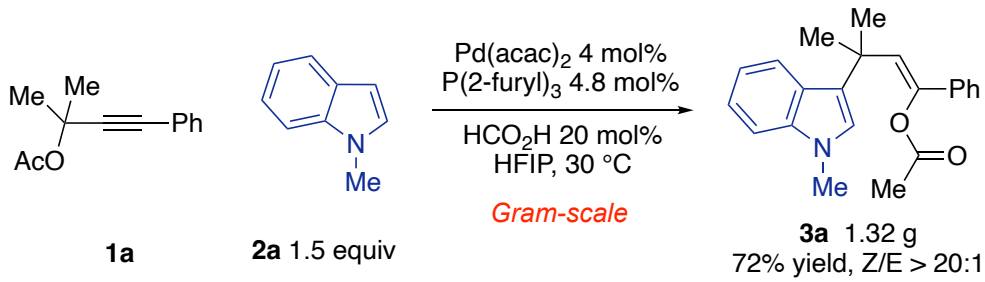
2-Methyl-4-phenylbut-3-yn-2-yl furan-2-carboxylate

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.56 (t, *J* = 0.9 Hz, 1H), 7.45-7.43 (m, 2H), 7.28-7.26 (m, 3H), 7.15 (d, *J* = 3.5 Hz, 1H), 6.48 (dd, *J* = 3.4, 1.6 Hz, 1H), 1.88 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 157.2, 146.2, 145.3, 132.0, 128.5, 128.3, 122.7, 117.8, 111.9, 89.8, 84.7, 73.9, 29.4.

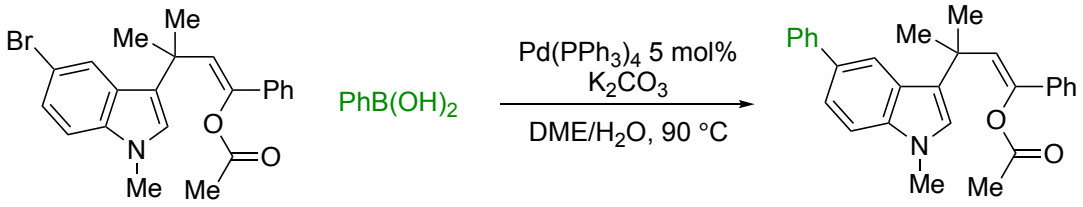
LC-MS (ESI): Calcd for $C_{16}H_{15}O_3$ $[M+H]^+$: 255.10; found: 255.17.

V. Scale-up synthesis and product derivatization



1a **2a** 1.5 equiv **3a** 1.32 g
72% yield, Z/E > 20:1

In an argon-filled glovebox, $Pd(acac)_2$ (67.0 mg, 0.22 mmol), $P(2\text{-furyl})_3$ (61.3 mg, 0.264 mmol) and 5.5 mL of HFIP were charged into an oven-dried 20-mL vial. After stirring for about 30 minutes at rt, *N*-methylindole (1.0 mL, 8.25 mmol), formic acid (42 μL, 1.1 mmol) and propargylic acetate **1a** (1.11 g, 5.5 mmol) were added sequentially to the reaction mixture. The vial was sealed with a screw cap and placed in a heating block maintained at 30 °C. After stirring for 24 hours, the crude reaction mixture was purified by flash chromatography on silica (ethyl acetate/hexanes 1:20) to afford **3a** in 72% yield (1.32 g, Z/E > 20:1).



3b **6a**

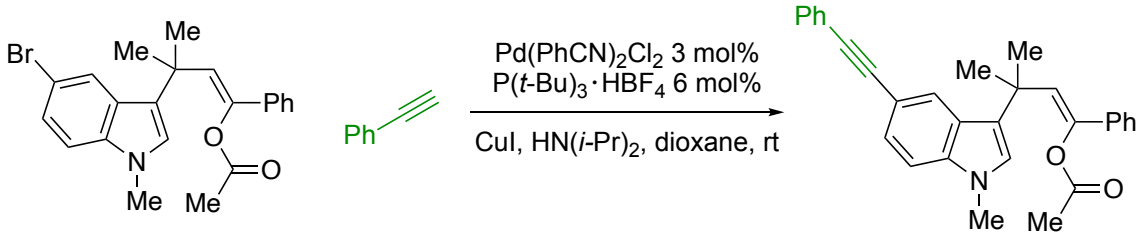
The reaction condition is modified based on the reported procedure.[5] To a 10-mL reaction tube in an argon-filled glove box, **3b** (41.2 mg, 0.1 mmol) and phenylboronic acid (18.3 mg, 0.15 mmol) were dissolved in DME/H_2O (0.8 mL/0.2 mL), followed by the addition of $Pd(PPh_3)_4$ (5.8 mg, 0.005 mmol) and potassium carbonate (27.6 mg, 0.2 mmol). The reaction tube was sealed with a screw cap and placed in a heating block maintained at 90 °C After stirring overnight, the reaction mixture was quenched with brine and extracted with ethyl acetate three times. The combined organic layers were then dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified on silica by flash chromatography (ethyl acetate/hexanes 1:5) as pale-yellow oil. 25 mg, 61% yield.

(*Z*)-3-Methyl-3-(1-methyl-5-phenyl-1*H*-indol-3-yl)-1-phenylbut-1-en-1-yl acetate (6a)

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.01 (s, 1H), 7.62 (d, J = 8.4 Hz, 2H), 7.48 (d, J = 8.5 Hz, 1H), 7.42-7.38 (m, 4H), 7.35 (d, J = 8.5 Hz, 1H), 7.30-7.27 (m, 3H), 7.25 (t, J = 7.4 Hz, 1H), 6.90 (s, 1H), 6.01 (s, 1H), 3.78 (s, 3H), 1.90 (s, 3H), 1.70 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 169.1, 145.2, 142.9, 137.4, 136.7, 132.2, 128.7, 128.6, 128.1, 127.6, 127.1, 126.4, 126.3, 125.3, 124.9, 123.9, 121.4, 119.8, 109.6, 36.0, 32.8, 29.4, 20.6.

HRMS (ESI): Calcd for $C_{28}H_{27}NO_2Na$ $[M+Na]^+$: 432.1934; found: 432.1937.



3b **6b**

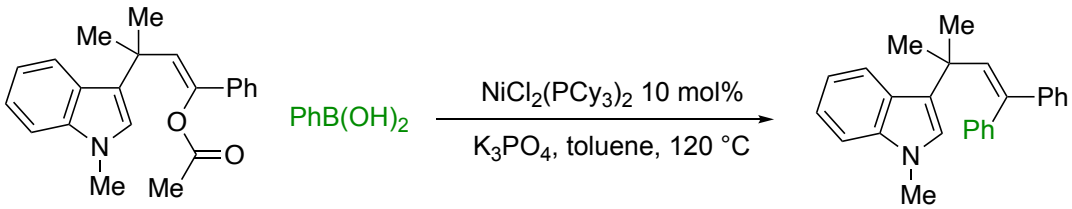
To a 10-mL reaction tube in an argon-filled glove box, **3b** (41.2 mg, 0.1 mmol), $Pd(PhCN)_2Cl_2$ (1.2 mg, 0.003 mmol), $P(t\text{-}Bu)_3 \cdot HBF_4$ (1.7 mg, 0.006 mmol), and CuI (0.4 mg, 0.002 mmol) were dissolved in dioxane (0.4 mL). Diisopropylamine (17 μL, 0.12 mmol) and phenylacetylene (13 μL, 0.12 mmol) were then added by microsyringe, and the reaction was stirred for 18 hours at rt. After complete consumption of **3b** (TLC monitoring), the solution was diluted with ethyl acetate and evaporated to dryness. The crude product was purified on silica by flash chromatography (ethyl acetate/hexanes 1:10) to give **6b** (34 mg, 78% yield) as yellow oil.

(*Z*)-3-Methyl-3-[1-methyl-5-(phenylethynyl)-1H-indol-3-yl]-1-phenylbut-1-en-1-yl acetate (6b)

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.96 (s, 1H), 7.54 (d, J = 8.5 Hz, 2H), 7.40-7.37 (m, 3H), 7.34-7.28 (m, 5H), 7.26-7.23 (m, 2H), 6.89 (s, 1H), 6.02 (s, 1H), 3.75 (s, 3H), 1.85 (s, 3H), 1.67 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 169.0, 145.3, 137.5, 136.4, 131.6, 128.6, 128.4, 128.2, 127.8, 126.6, 126.1, 125.8, 125.3, 125.1, 124.9, 124.2, 123.8, 113.2, 109.5, 91.6, 87.1, 35.8, 32.8, 29.5, 20.5.

HRMS (ESI): Calcd for $C_{30}H_{27}NO_2Na$ $[M+Na]^+$: 456.1934; found: 456.1933.



3a **6c**

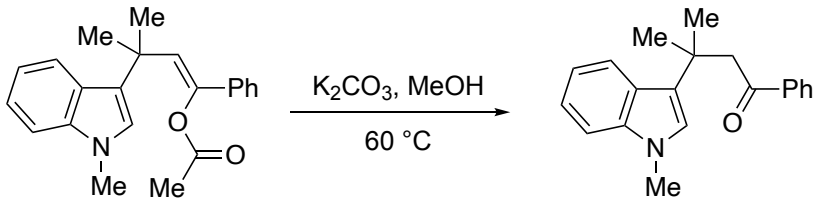
The compound is prepared according to the reported procedure with some modifications.[6] In an argon-filled glove box, $Ni(PCy_3)_2Cl_2$ (6.9 mg, 0.01 mmol), phenyl boronic acid (61.0 mg, 0.5 mmol) and K_3PO_4 (191.0 mg, 0.9 mmol) were charged into a dry 10-mL Schlenk tube, followed by the addition of **3a** (33.3 mg, 0.1 mmol) and toluene (1 mL). The reaction mixture was sealed tightly with a Teflon-lined screw cap and stirred on a hotplate maintained at 120 °C for 48 h. After cooling down to room temperature, the crude product was purified on silica by flash chromatography (ethyl acetate/hexanes 1:70) to give **6c** (20 mg, 57% yield) as colorless oil.

1-Methyl-3-(2-methyl-4,4-diphenylbut-3-en-2-yl)-1H-indole (6c)

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.74 (d, J = 7.9 Hz, 1H), 7.24-7.17 (m, 7H), 7.11 (t, J = 7.4 Hz, 1H), 7.06 (t, J = 7.2 Hz, 1H), 7.01-6.99 (m, 2H), 6.68 (d, J = 7.4 Hz, 2H), 6.56 (s, 1H), 6.38 (s, 1H), 3.57 (s, 3H), 1.52 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 144.0, 140.7, 140.1, 139.1, 137.7, 129.8, 128.1, 127.1, 126.9, 126.8, 126.7, 126.0, 124.9, 124.2, 121.4, 121.1, 118.4, 109.1, 36.8, 32.4, 30.7.

LC-MS (ESI): Calcd for $C_{26}H_{25}NNa$ $[M+Na]^+$: 374.19; found: 374.27.



3a **6d**

To a mixture of **3a** (33.3 mg, 0.1 mmol) and K_2CO_3 (16.6 mg, 0.12 mmol) was added dry MeOH (0.5 mL). After stirring at 60 °C for 2 hours, the reaction mixture was cooled to room temperature and concentrated under reduced pressure. The product **6d** was then purified by silica gel chromatography (ethyl acetate/hexanes 1:60) as colorless oil. 26 mg, 89% yield.

3-Methyl-3-(1-methyl-1H-indol-3-yl)-1-phenylbutan-1-one (6d)

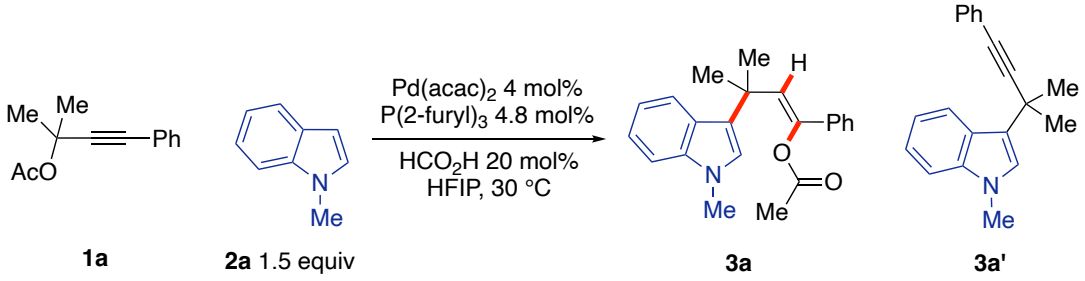
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.83 (d, J = 8.1 Hz, 1H), 7.76 (d, J = 7.8 Hz, 2H), 7.44 (t, J = 7.4 Hz, 1H), 7.30-7.25 (m, 3H), 7.20 (t, J = 7.6 Hz, 1H), 7.10 (t, J = 7.5 Hz, 1H), 6.76 (s, 1H), 3.68 (s, 3H), 3.46 (s, 2H), 1.61 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 200.4, 138.6, 137.9, 132.5, 128.3, 128.2, 126.1, 125.4, 123.4. 121.3, 121.0, 118.6, 109.7, 49.6, 34.9, 32.7, 28.8.

HRMS (ESI): Calcd for $C_{20}H_{21}NONa$ $[M+Na]^+$: 314.1515; found: 314.1517.

VI. Mechanistic studies

Table S6. Control experiments

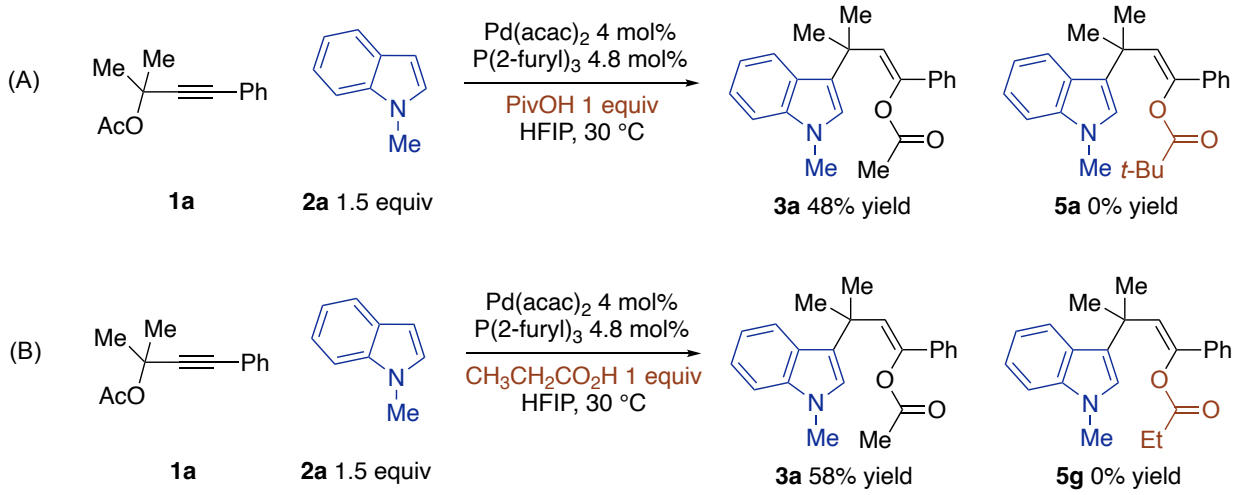


1a **2a** 1.5 equiv **3a** **3a'**

entry	variations from standard conditions	conversion of **1a**	yield of **3a**	yield of **3a′**
1	none	100%	86%	0%
2	without palladium catalyst	100%	0%	49%
3	without phosphine ligand	100%	25%	30%
4	without HCO_2H	100%	54%	20%
5	without $Pd(acac)_2$ and $P(2\text{-furyl})_3$	100%	0%	56%
6	without $Pd(acac)_2$, $P(2\text{-furyl})_3$ and HCO_2H	100%	0%	58%

1-Methyl-3-(2-methyl-4-phenylbut-3-yn-2-yl)-1*H*-indole (3a′) [1084888-36-7][7]

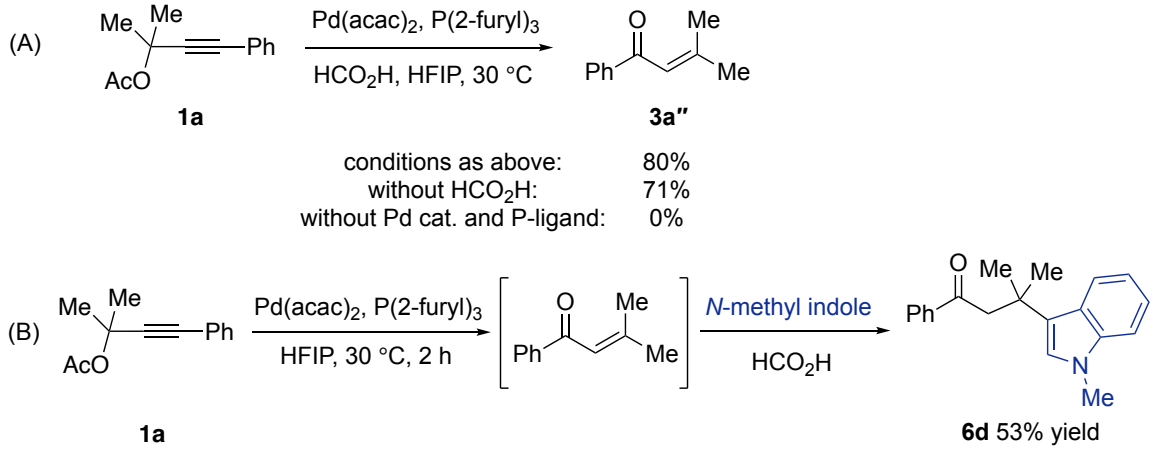
^{1}H NMR (600 MHz, $CDCl_3$): δ 8.01 (d, J = 7.8 Hz, 1H), 7.44 (d, J = 5.4 Hz, 2H), 7.32 (d, J = 8.3 Hz, 1H), 7.29-7.24 (m, 4H), 7.14 (t, J = 7.5 Hz, 1H), 7.01 (s, 1H), 3.76 (s, 3H), 1.82 (s, 6H).



Scheme S1. Competition study of acyloxylation process

General procedure of the reaction shown in Scheme S1: in an argon-filled glovebox, $Pd(acac)_2$ (1.2 mg, 0.004 mmol), $P(2\text{-furyl})_3$ (1.1 mg, 0.0048 mmol) and 0.1 mL of HFIP were charged into an oven-dried 4-mL vial. After stirring for about 15 minutes at rt, *N*-methylindole (19 μL, 0.15 mmol), carboxylic acid (0.1 mmol) and propargylic acetate **1a** (20.2 mg, 0.1 mmol) were added sequentially to the reaction mixture. The vial was sealed with a screw cap and placed in a heating block maintained at 30 °C. After stirring for 24 hours, the crude reaction mixture was purified by flash chromatography on silica (ethyl acetate/hexanes 1:60).

Result: The exclusive formation of enol acetate **3a** indicated that acyloxylation of alkynyl moiety on **1a** is an intramolecular process.



Scheme S2. Investigation of side-reaction pathways

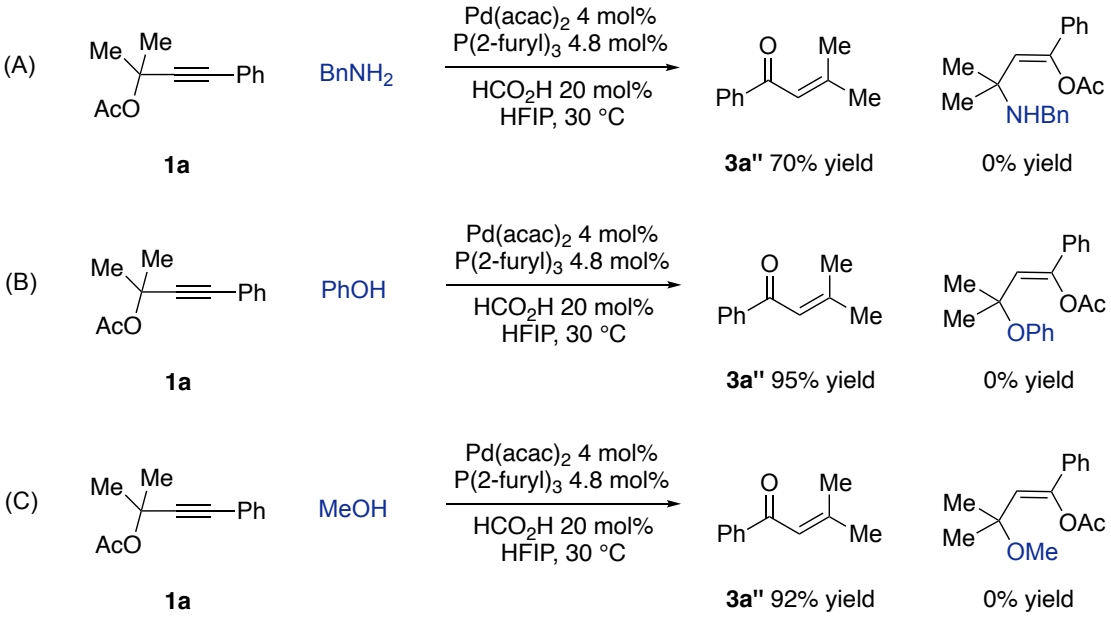
General procedure of the reaction shown in Scheme S2-A: in an argon-filled glovebox, $Pd(acac)_2$ (1.2 mg, 0.004 mmol), $P(2\text{-furyl})_3$ (1.1 mg, 0.0048 mmol) and 0.1 mL of HFIP were charged into an oven-dried 4-mL vial. After stirring for about 15 minutes at rt, formic acid (0.8 μL, 0.02 mmol) and propargylic acetate **1a** (20.2 mg, 0.1 mmol) were added sequentially to the reaction mixture. The vial was sealed with a screw cap and placed in a

heating block maintained at 30 °C. After stirring for two hours, aliquots from the reaction mixture were evaluated by GC-MS. The crude product was then purified by flash chromatography on silica (ethyl acetate/hexanes 1:10), affording **3a′′** in 80% yield as yellow oil. For a control experiment without palladium catalyst and phosphine ligand, no enone product (**3a′′**) was detected based on the crude ^{1}H-NMR.

3-Methyl-1-phenylbut-2-en-1-one (3a′′) [5650-07-7][8]

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.94-7.92 (m, 2H), 7.53-7.50 (m, 1H), 7.46-7.43 (m, 2H), 6.75 (hept, J = 1.3 Hz, 1H), 2.21 (s, 3H), 2.02 (s, 3H).

General procedure of the reaction shown in Scheme S2-B: in an argon-filled glovebox, $Pd(acac)_2$ (1.2 mg, 0.004 mmol), $P(2\text{-furyl})_3$ (1.1 mg, 0.0048 mmol) and 0.1 mL of HFIP were charged into an oven-dried 4-mL vial. After stirring for about 15 minutes at rt, propargylic acetate **1a** (20.2 mg, 0.1 mmol) was added, and the resulting solution stirred at 30 °C for 2 h. Afterwards, *N*-methylindole (19 μL, 0.15 mmol) and formic acid (0.8 μL, 0.02 mmol) were added sequentially. The vial was sealed with a screw cap and placed in a heating block maintained at 30 °C. After stirring for 24 hours, the crude reaction mixture was purified by flash chromatography on silica (ethyl acetate/hexanes 1:60), affording **6d** in 53% yield as colorless oil.



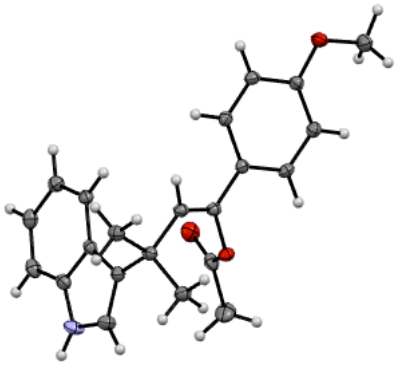
Scheme S3. The reactivity of propargylic acetate **1a** with other nucleophiles under the standard conditions

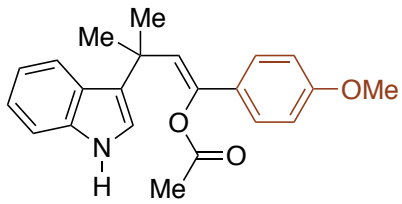
General procedure of the reaction shown in Scheme S3: in an argon-filled glovebox, $Pd(acac)_2$ (1.2 mg, 0.004 mmol), $P(2\text{-furyl})_3$ (1.1 mg, 0.0048 mmol) and 0.1 mL of HFIP were charged into an oven-dried 4-mL vial. After stirring for about 15 minutes at rt, nucleophile (0.15 mmol), formic acid (0.8 μL, 0.02 mmol) and propargylic acetate **1a** (20.2 mg, 0.1 mmol) were added sequentially to the reaction mixture. The vial was sealed with a screw cap and placed in a heating block maintained at 30 °C. After stirring for 24 hours, the crude reaction mixture was purified by flash chromatography on silica (ethyl acetate/hexanes 1:60).

VII. X-ray crystallographic data

Deposition number CCDC 2221866

ORTEP of **4a**, thermal ellipsoids are shown at 50% probability.





Bond precision: C-C = 0.0029 A Wavelength=0.71073

Cell: a=7.9756(3) b=11.0244(4) c=20.3840(8)
alpha=90 beta=90 gamma=90
Temperature: 100 K

	Calculated	Reported
Volume	1792.29(12)	1792.29(12)
Space group	P 21 21 21	P 21 21 21
Hall group	P 2ac 2ab	P 2ac 2ab
Moiety formula	C22 H23 N O3	?
Sum formula	C22 H23 N O3	C22 H23 N O3
Mr	349.41	349.41
Dx,g cm-3	1.295	1.295
Z	4	4
Mu (mm-1)	0.086	0.086
F000	744.0	744.0
F000'	744.34	
h,k,lmax	11,15,29	11,15,29
Nref	5726[3241]	5707
Tmin,Tmax	0.976,0.981	0.820,0.980
Tmin'	0.976	

Correction method= # Reported T Limits: Tmin=0.820 Tmax=0.980
AbsCorr = MULTI-SCAN

Data completeness= 1.76/1.00 Theta(max)= 31.020

R(reflections)= 0.0467(4383) wR2(reflections)= 0.1082(5707)

S = 1.047 Npar= 239

VIII. Reference

(1) Jiao, Z.; Shi, Q.; Zhou, J. S. Asymmetric Intermolecular Heck Reaction of Propargylic Acetates and Cycloalkenes to Access Fused Cyclobutenes. *Angew. Chem. Int. Ed.* **2017**, *56*, 14567-14571.

(2) Lu, Q.; Liu, K.; Zhang, H.; Du, Z.; Wang, X.; Wang, F. From Tunneling to Hopping: A Comprehensive Investigation of Charge Transport Mechanism in Molecular Junctions Based on Oligo(p-phenylene ethynylene)s. *ACS Nano* **2009**, *3*, 3861-3868.

(3) Manoni, E.; Daka, M.; Mastandrea, M. M.; Nisi, A. D.; Monari, M.; Bandini, M. Catalytic α-Allylation of Enones with Alcohols via [Gold(I)]-Mediated [3,3]-Sigmatropic Rearrangement of Propargylic Carboxylates. *Adv. Synth. Catal.* **2016**, *358*, 1404-1409.

(4) Okamoto, N.; Sueda, T.; Minami, H.; Miwa, Y.; Yanada, R. Regioselective Iodoazidation of Alkynes: Synthesis of α,α-Diazidoketones. *Org. Lett.* **2015**, *17*, 1336-1339.

(5) Dudhe, P.; Krishnan, M. A.; Yadav, K.; Roy, D.; Venkatasubbaiah, K.; Pathak, B.; Chelvam, V. Synthesis of 1-Indolyl-3,5,8-substituted γ-carbolines: One-Pot Solvent-Free Protocol and Biological Evaluation. *Beilstein J. Org. Chem*. **2021**, *17*, 1453-1463.

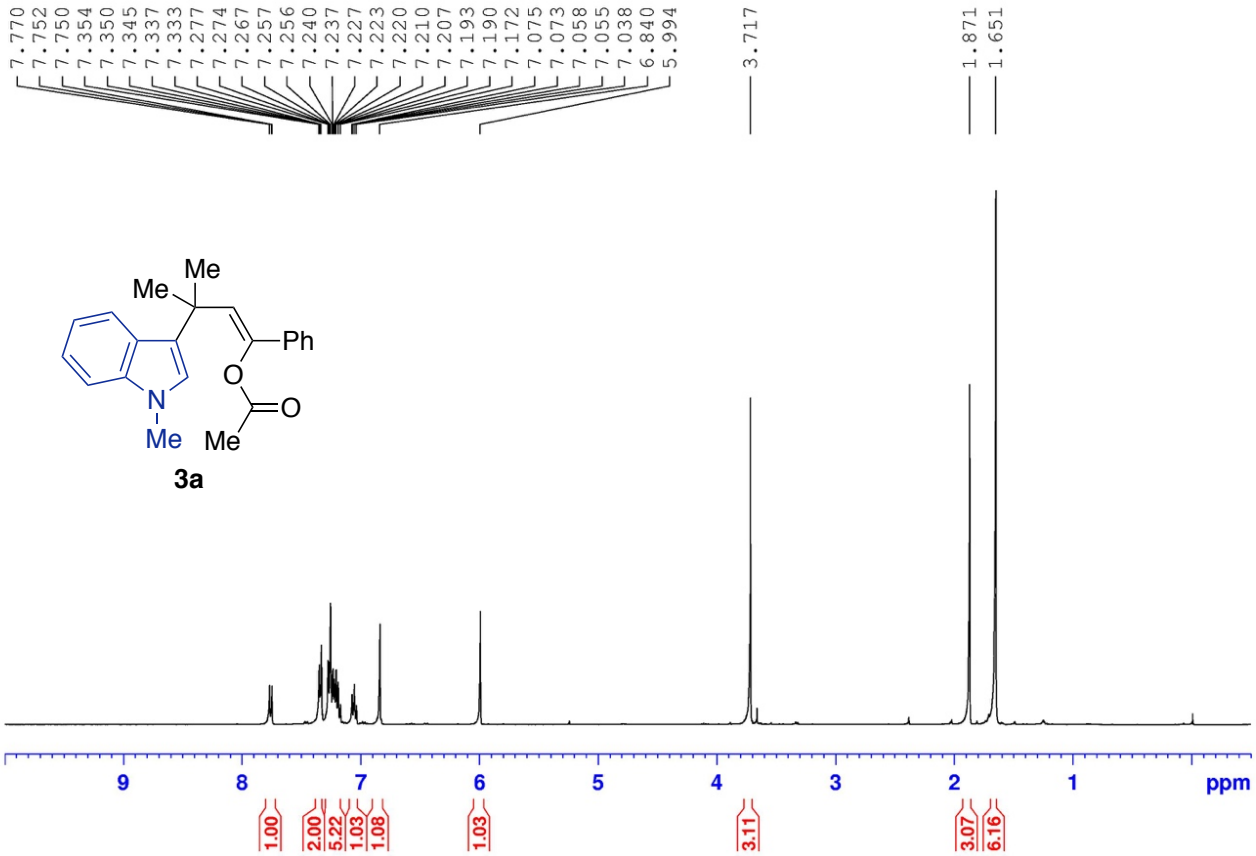
(6) Sun, C.-L.; Wang, Y.; Zhou, X.; Wu, Z.-H.; Li, B.-J.; Guan, B.-T.; Shi, Z.-J. Construction of Polysubstituted Olefins through Ni-Catalyzed Direct Activation of Alkenyl C–O of Substituted Alkenyl Acetates. *Chem. Eur. J.* **2010**, *16*, 5844-5847.

(7) Sanz, R.; Miguel, D.; Martínez, A.; Gohain, M.; García-García, P.; Fernández-Rodríguez, M. A.; Álvarez, E.; Rodríguez, F. Brønsted Acid Catalyzed Alkylation of Indoles with Tertiary Propargylic Alcohols: Scope and Limitations. *Euro. J. Org. Chem.* **2010**, *2010*, 7027-7039.

(8) Bermejo-López, A.; Kong, W.-J.; Tortajada, P. J.; Posevins, D.; Martín-Matute, B.; Bäckvall, J.-E. Iron-Catalyzed Borylation of Propargylic Acetates for the Synthesis of Multisubstituted Allenylboronates. *Chem. Eur. J.* **2023**, *29*, e202203130.

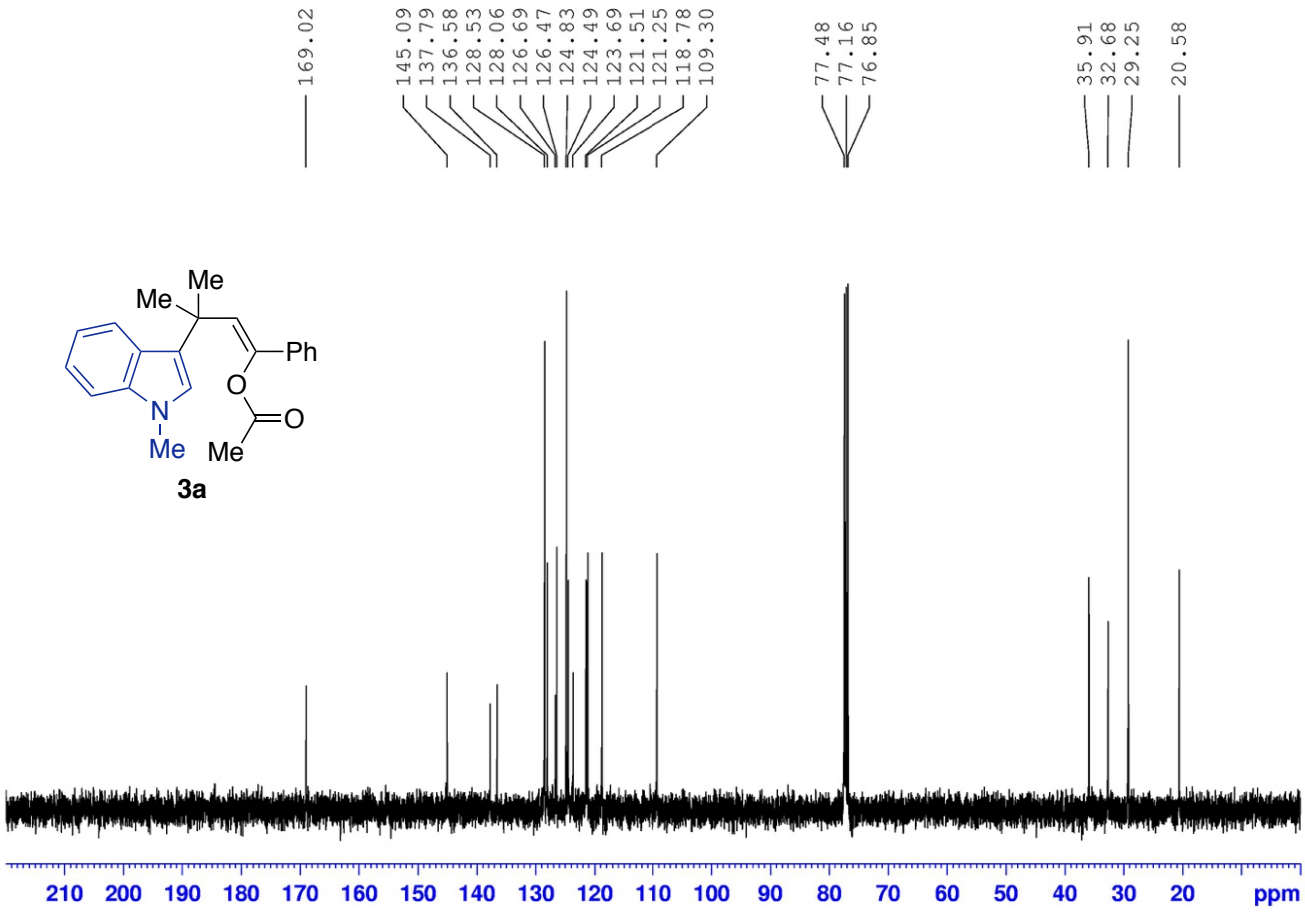
IX. NMR spectra

TSH-N5-301 AV400 1H



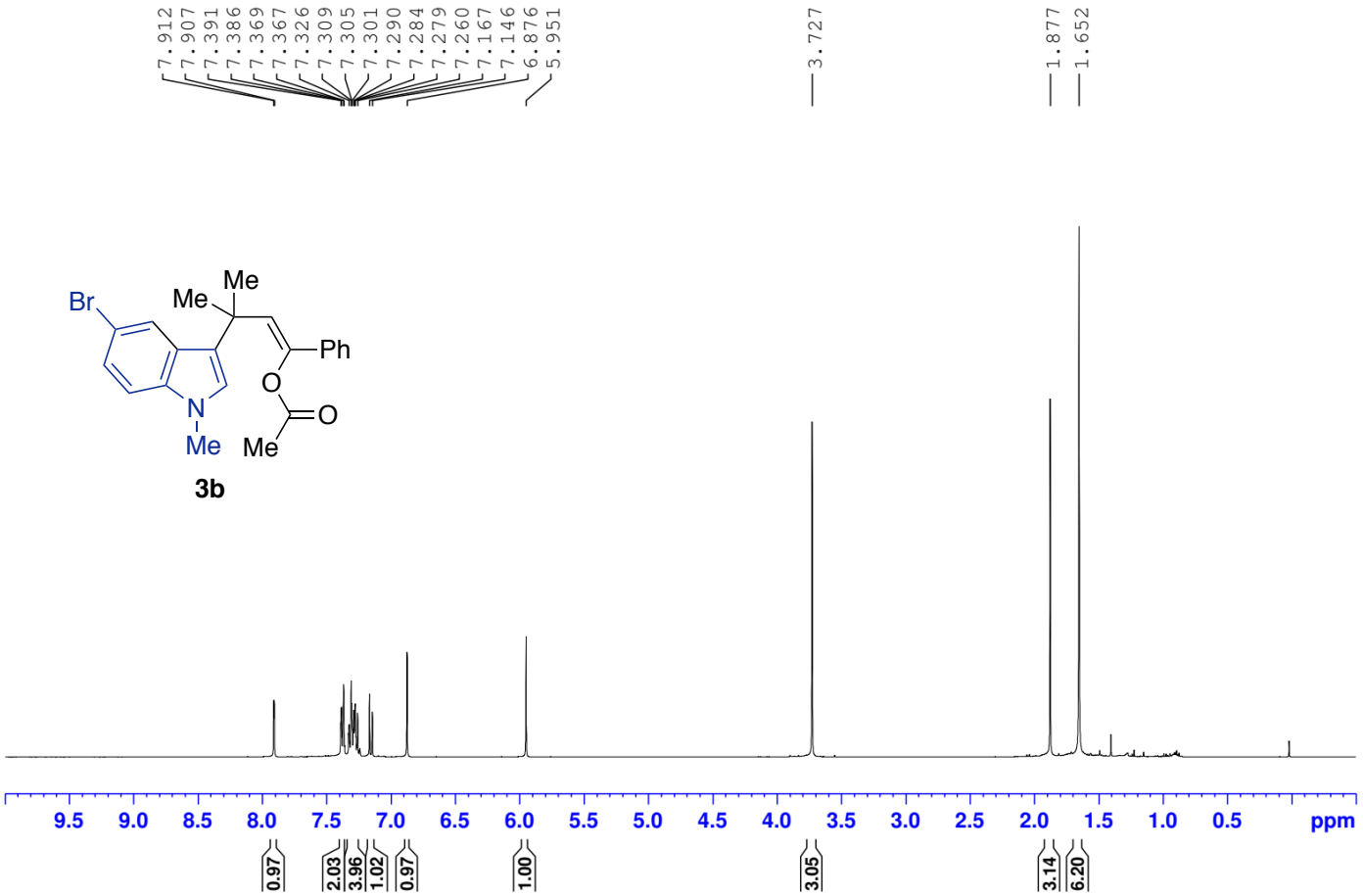
3a

TSH-N5-301 AV400 13C

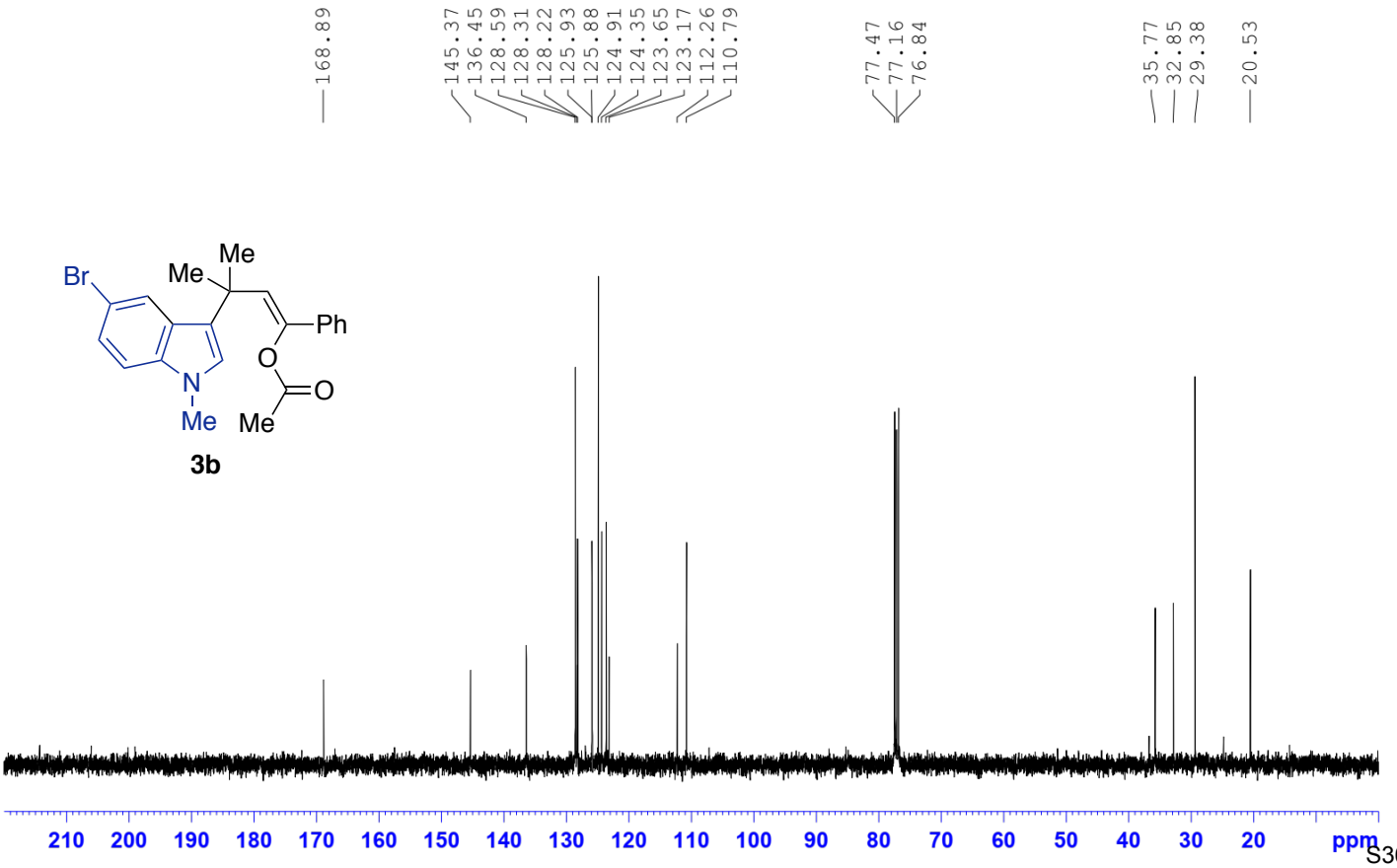


3a

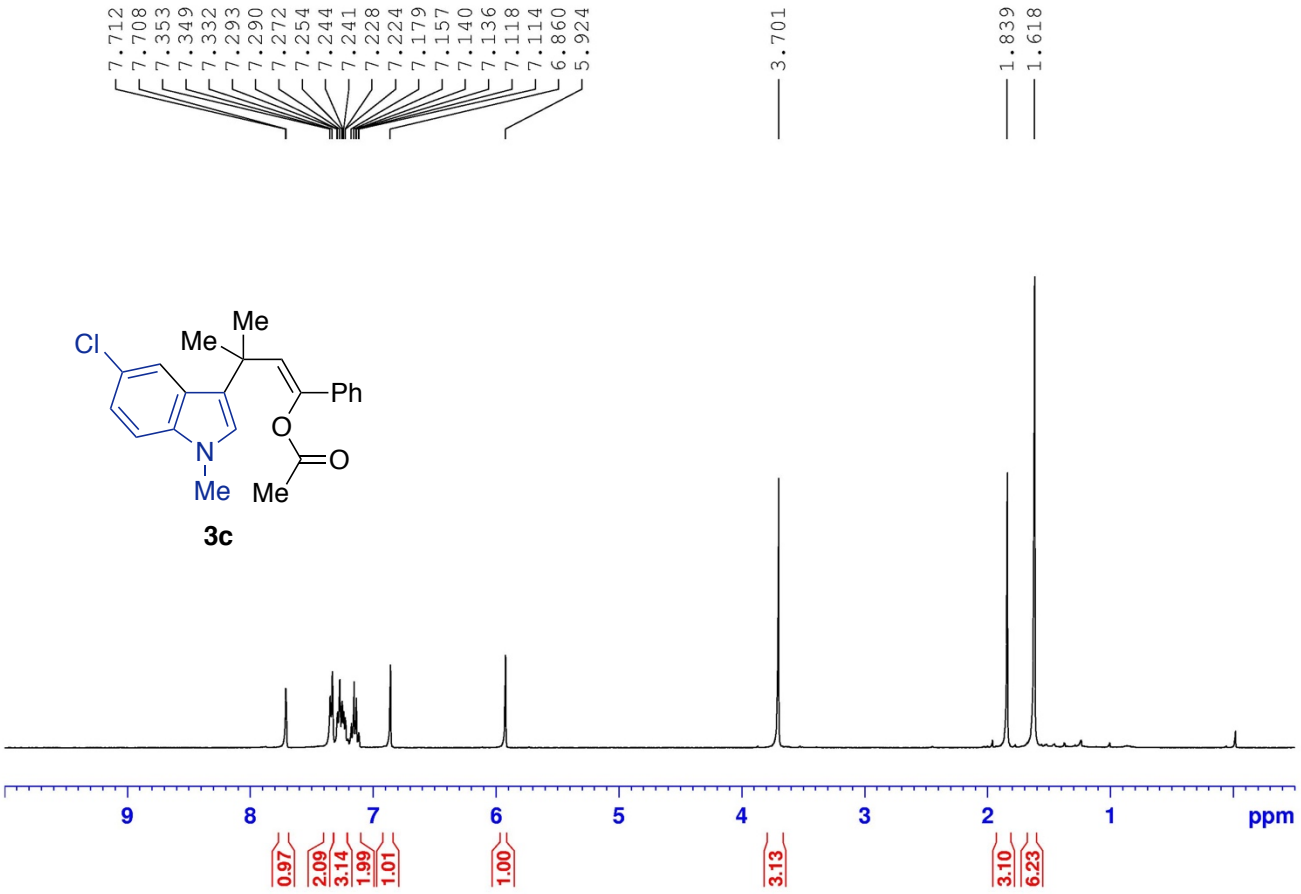
TSH-N6-75-8 1H



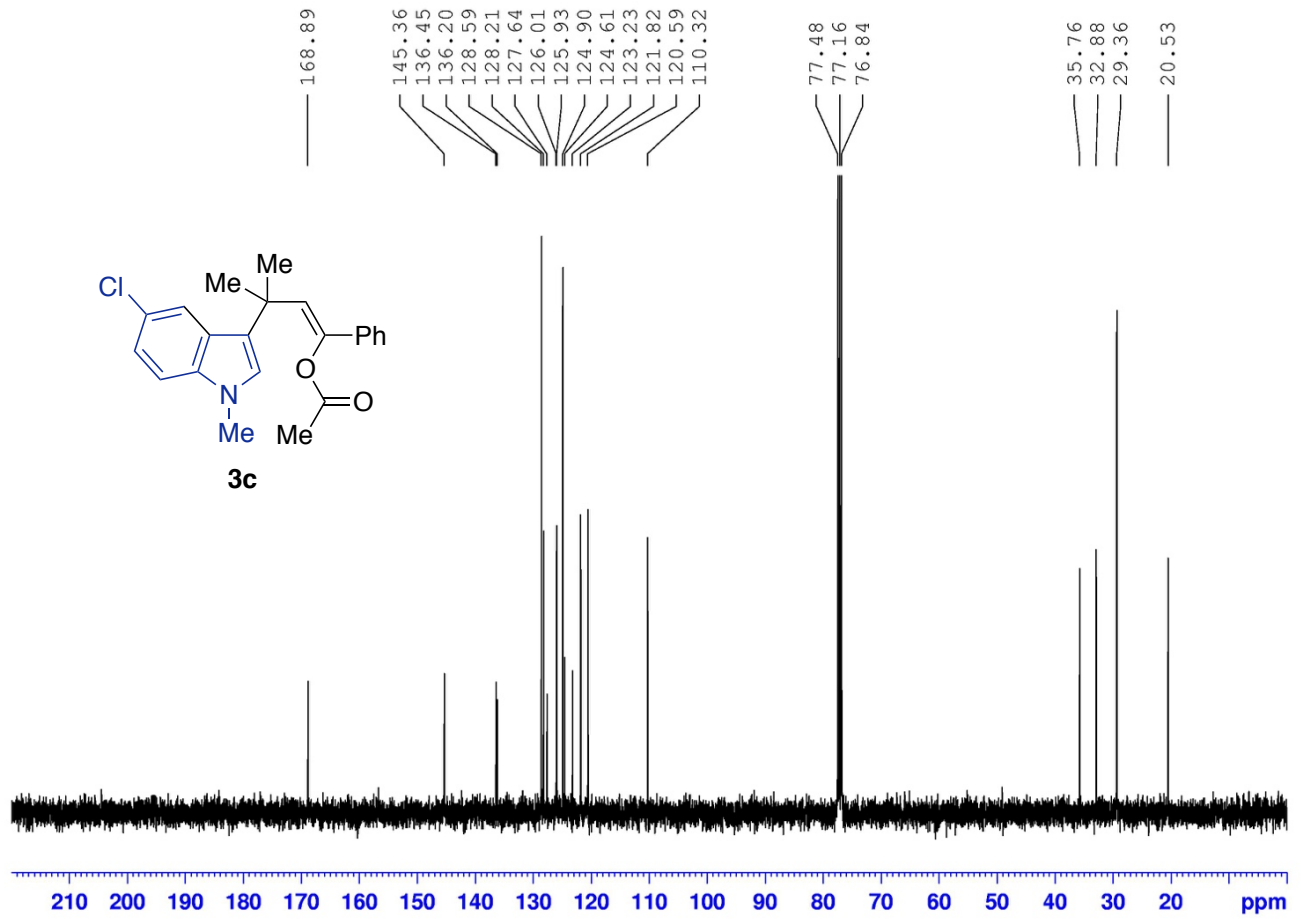
TSH-N6-75-8 13C



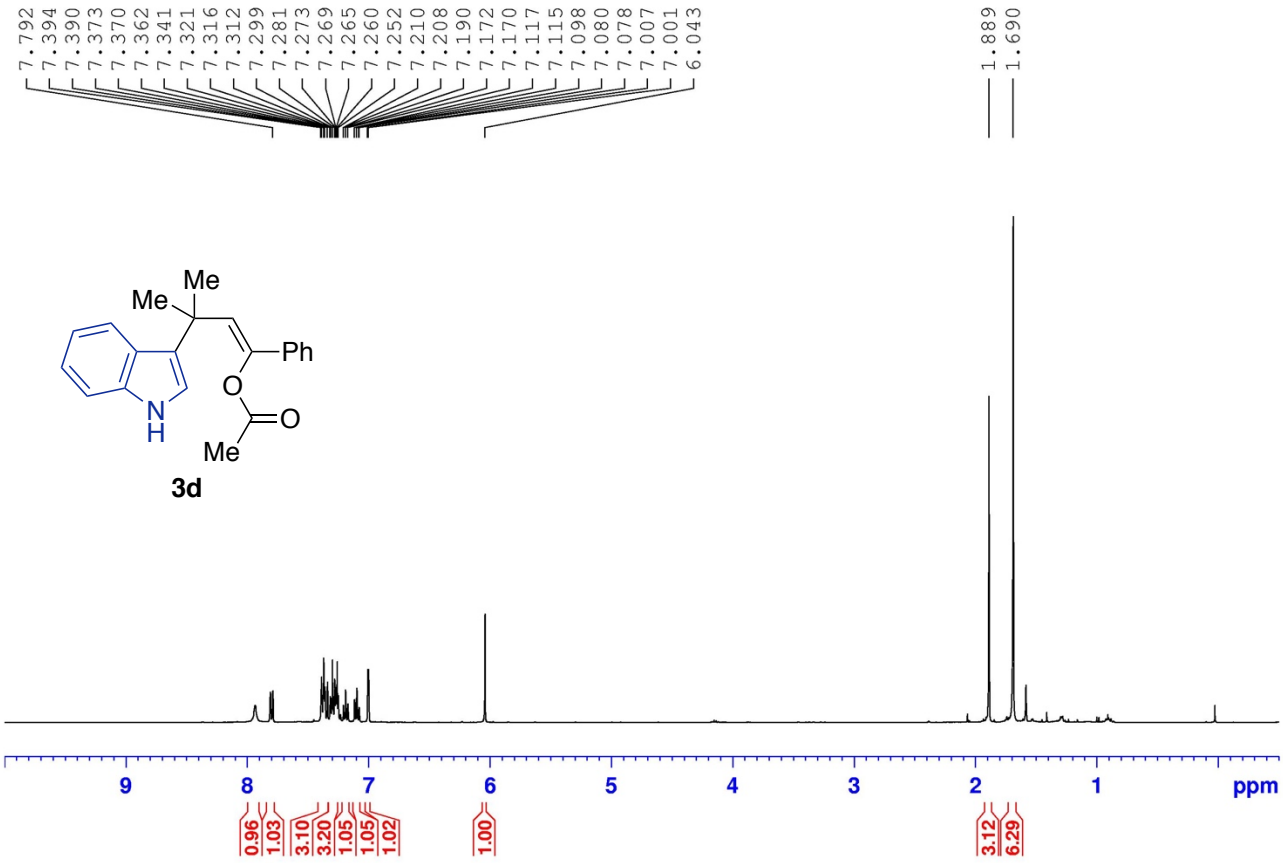
TSH-N5-59-6 1H



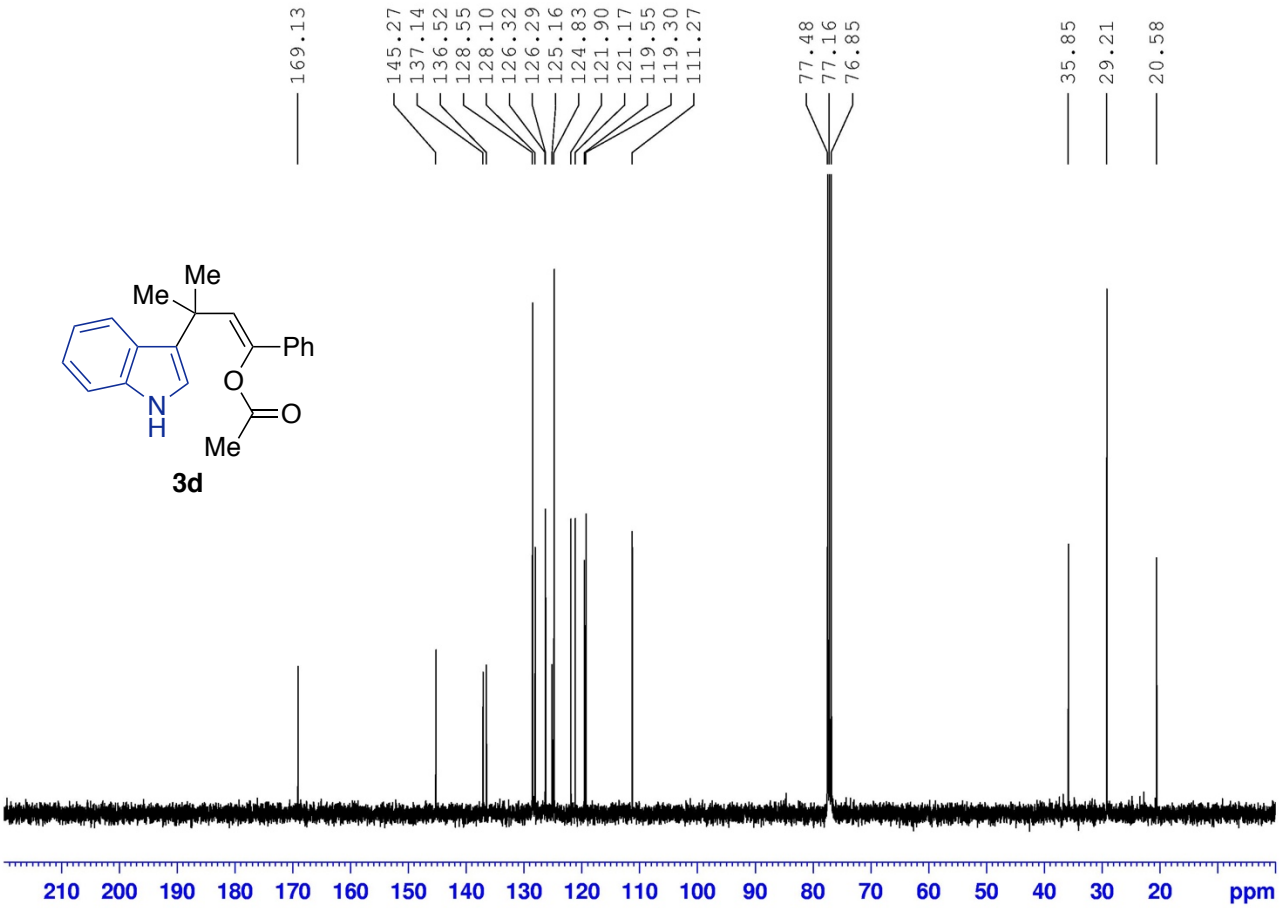
TSH-N5-59-6 13C

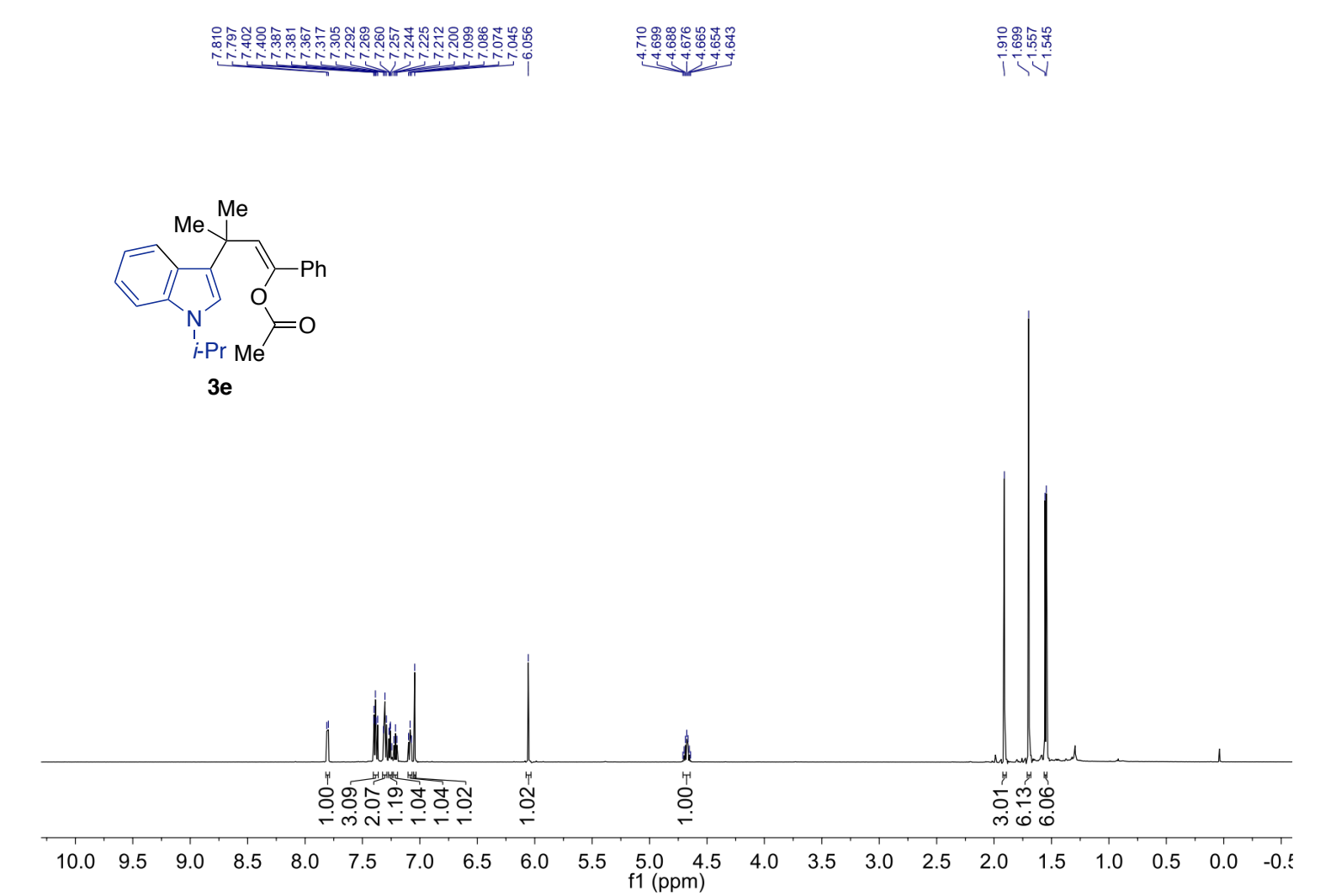


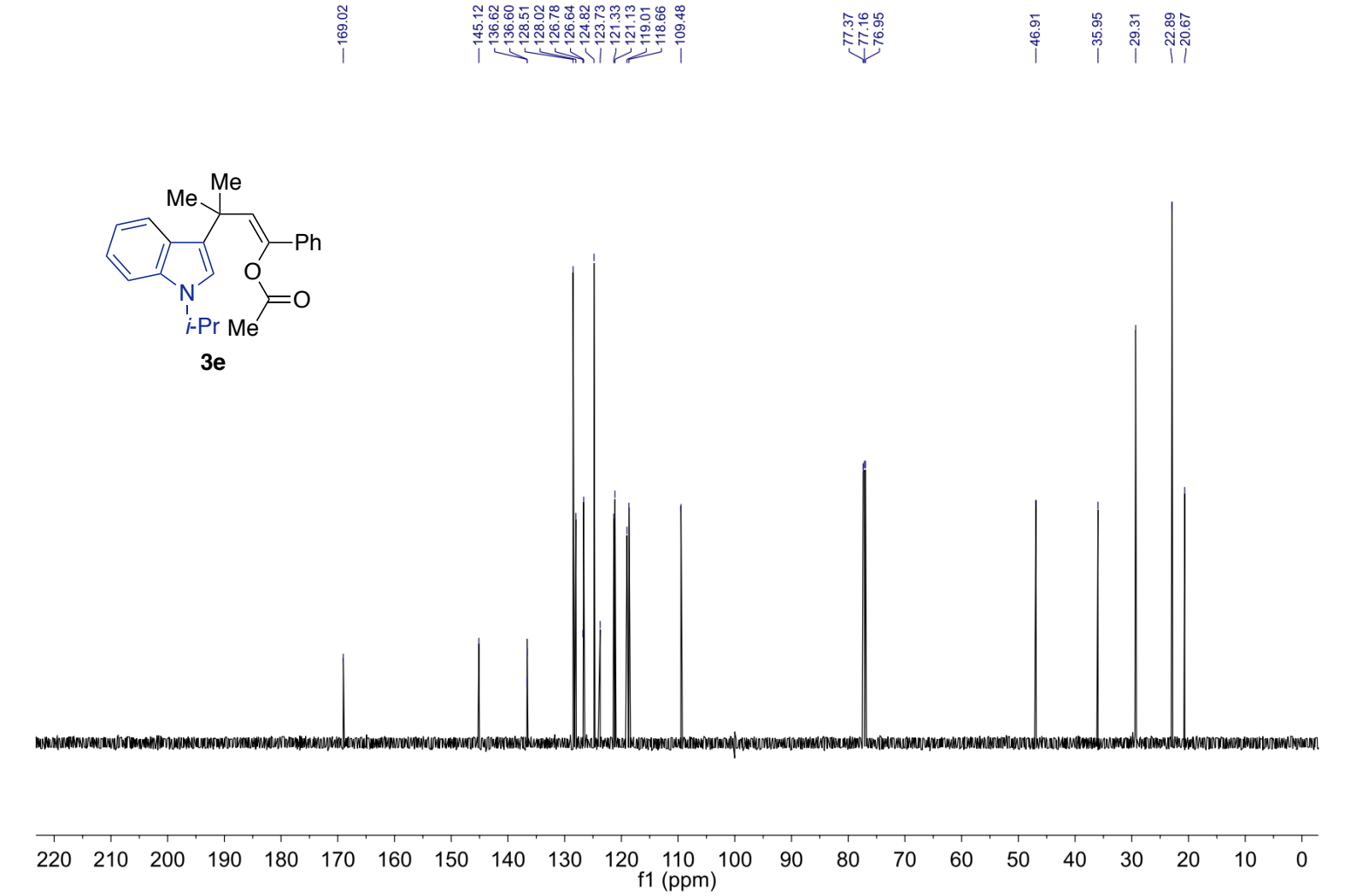
TSH-N5-73-4 1H



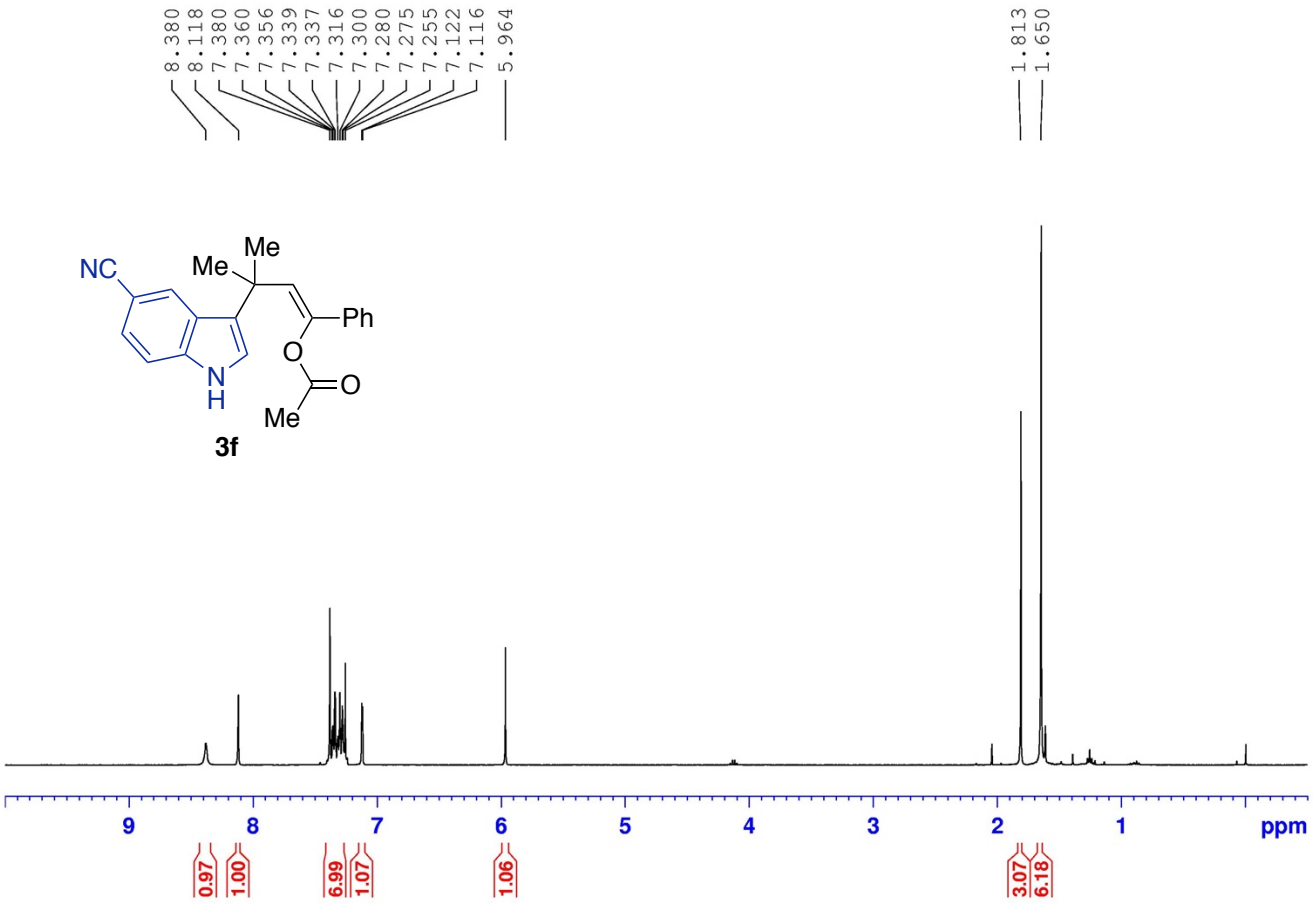
TSH-N5-73-4 13C



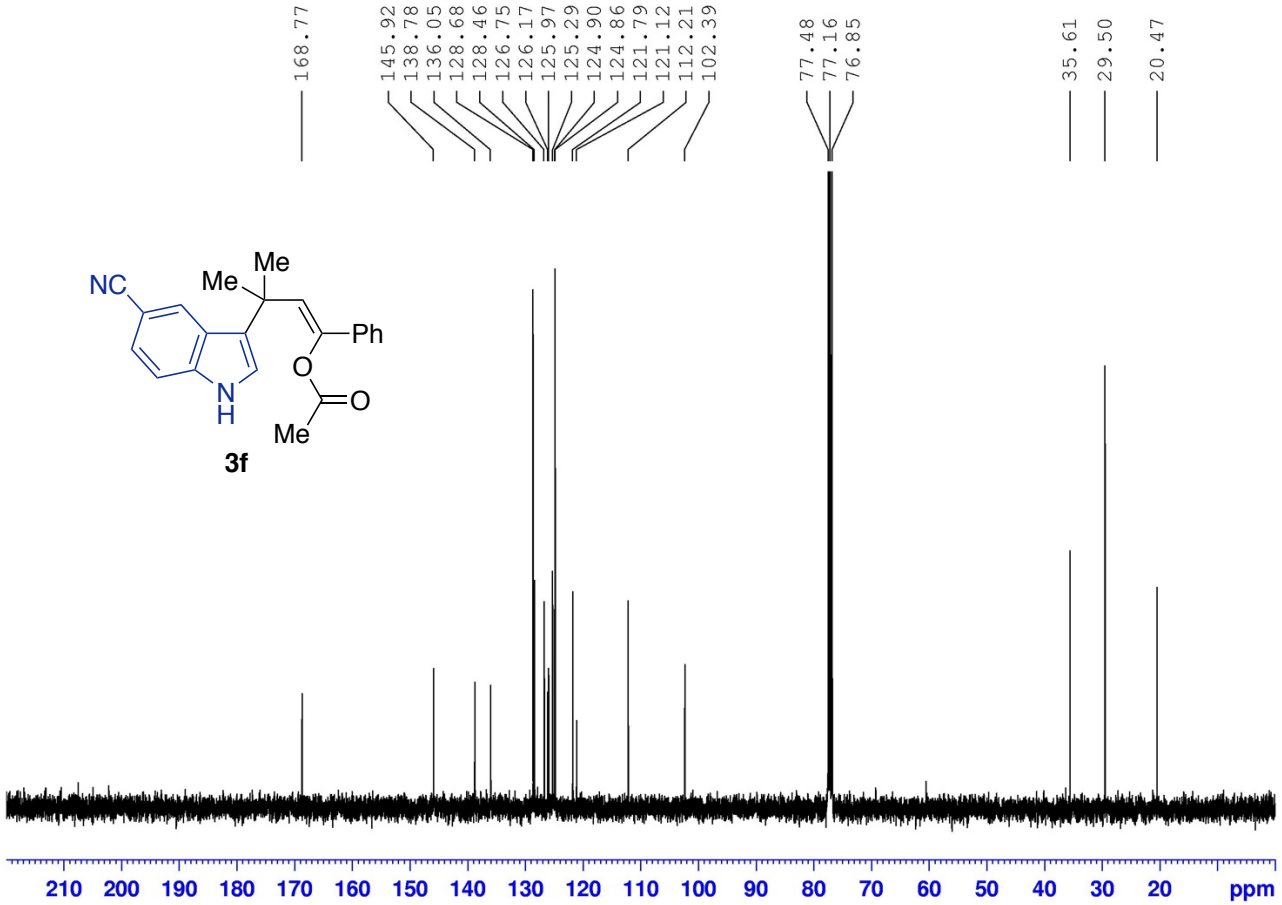

7.810
7.797
7.402
7.400
7.387
7.381
7.367
7.317
7.305
7.292
7.269
7.260
7.257
7.244
7.225
7.212
7.200
7.099
7.086
7.074
7.045
6.056
4.710
4.699
4.688
4.676
4.665
4.654
4.643
1.910
1.699
1.557
1.545
Me
Me
Ph
O
O
N
i-Pr
Me
3e
1.00
3.09
2.07
1.19
1.04
1.04
1.02
1.02
1.00
3.01
6.13
6.06
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


169.02
145.12
136.62
136.60
128.51
128.02
126.78
126.64
124.82
123.73
121.33
121.13
119.01
118.66
109.48
77.37
77.16
76.95
46.91
35.95
29.31
22.89
20.67
Me
Me
Ph
O
O
N
i-Pr
Me
3e
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

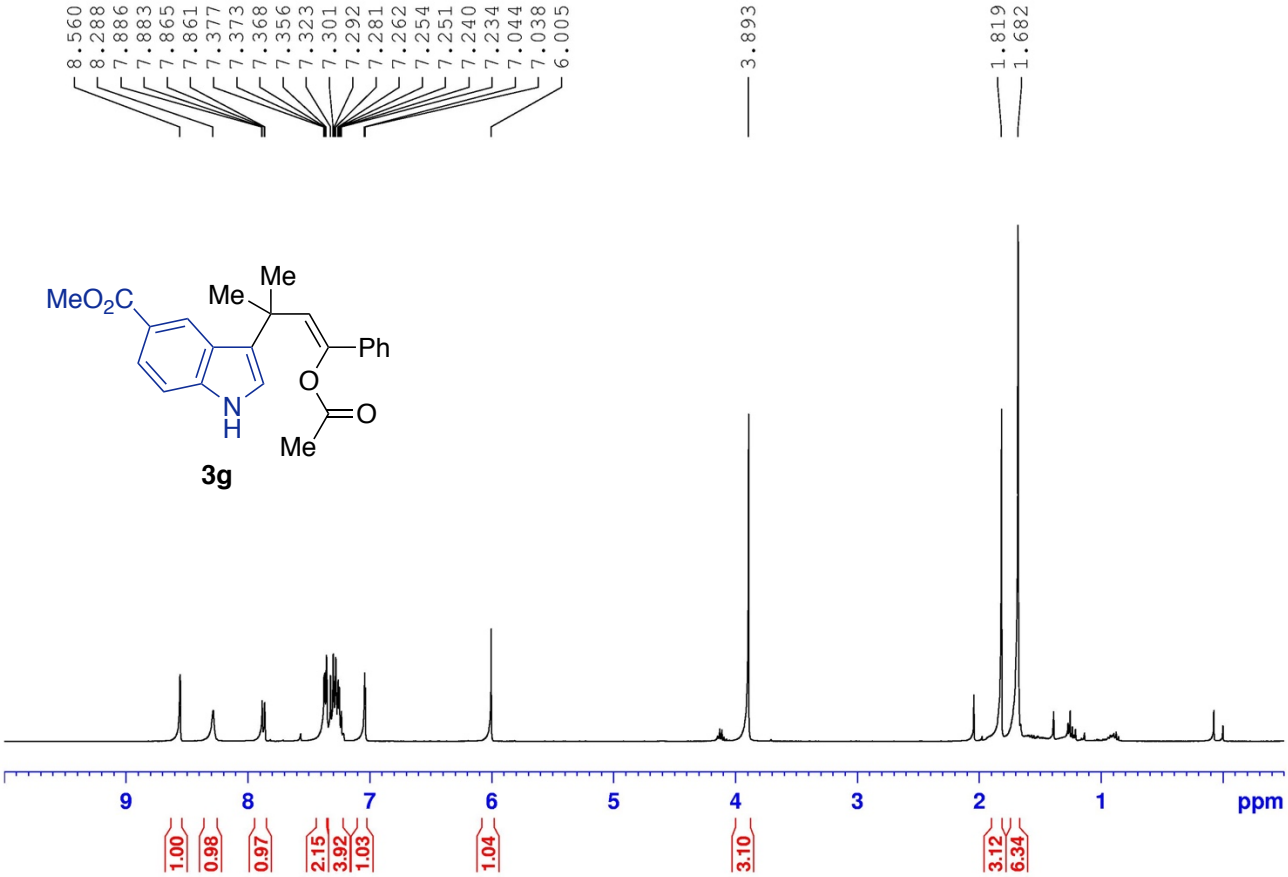
TSH-N6-87-10 1H



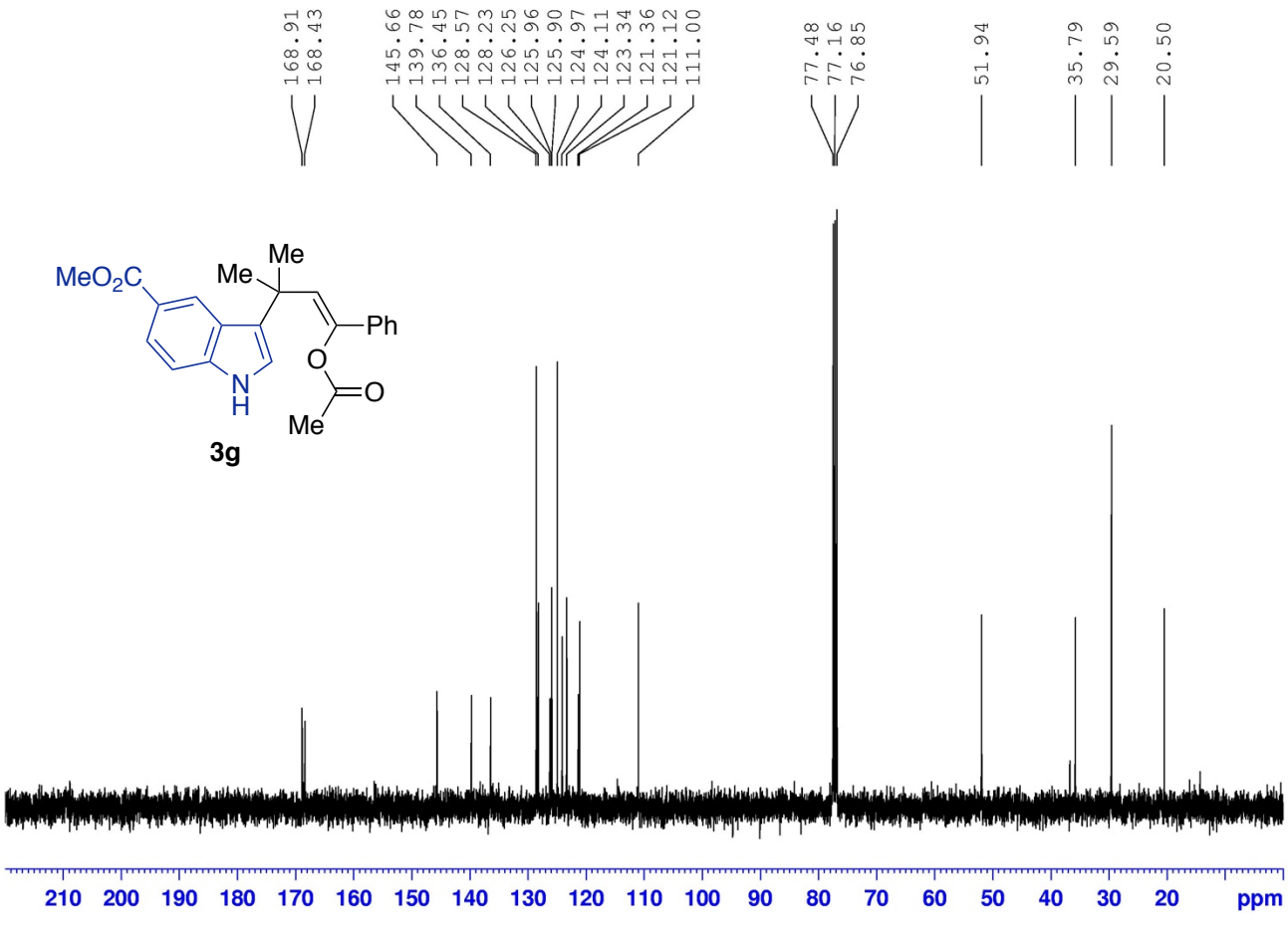
TSH-N6-87-10 13C

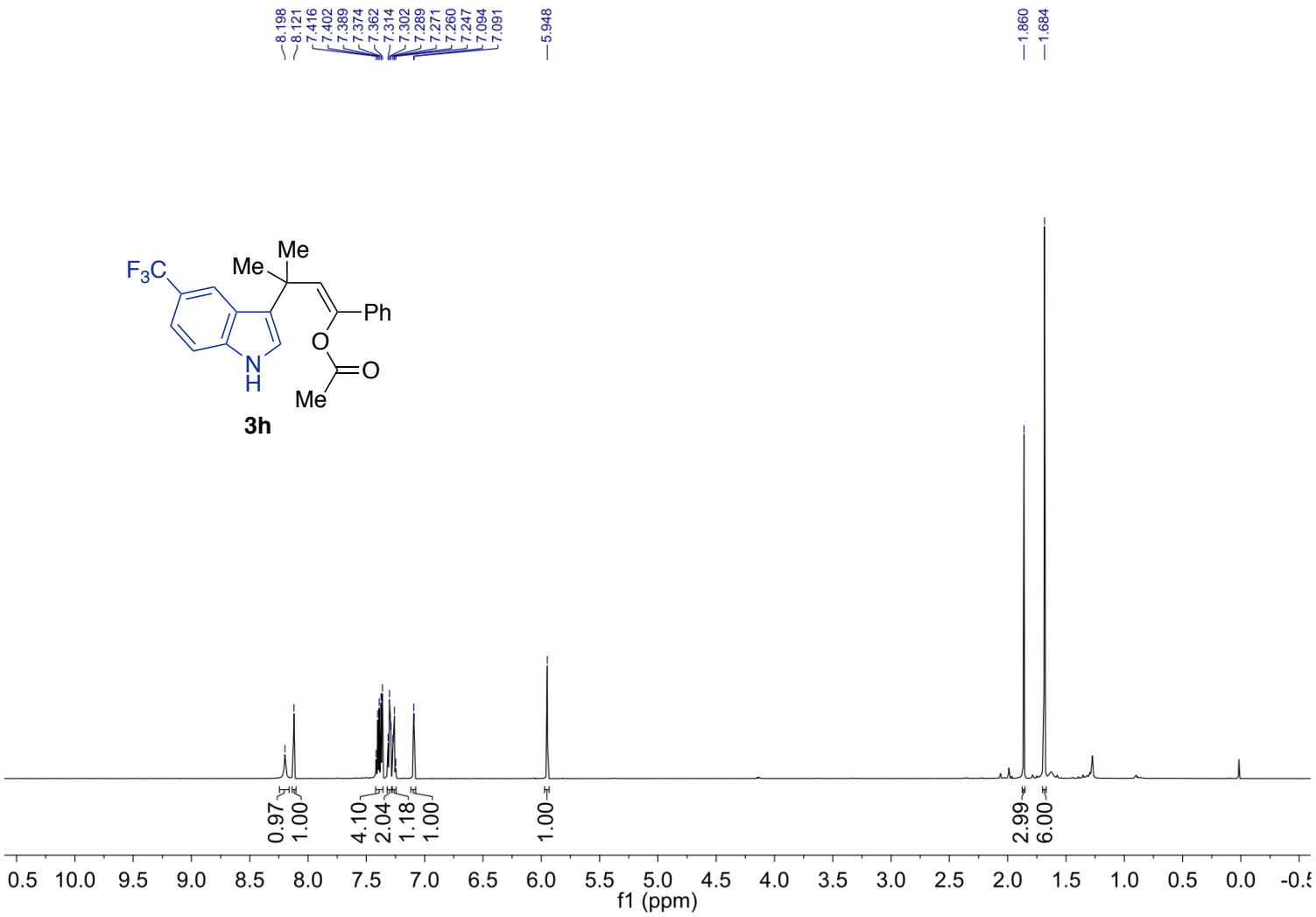


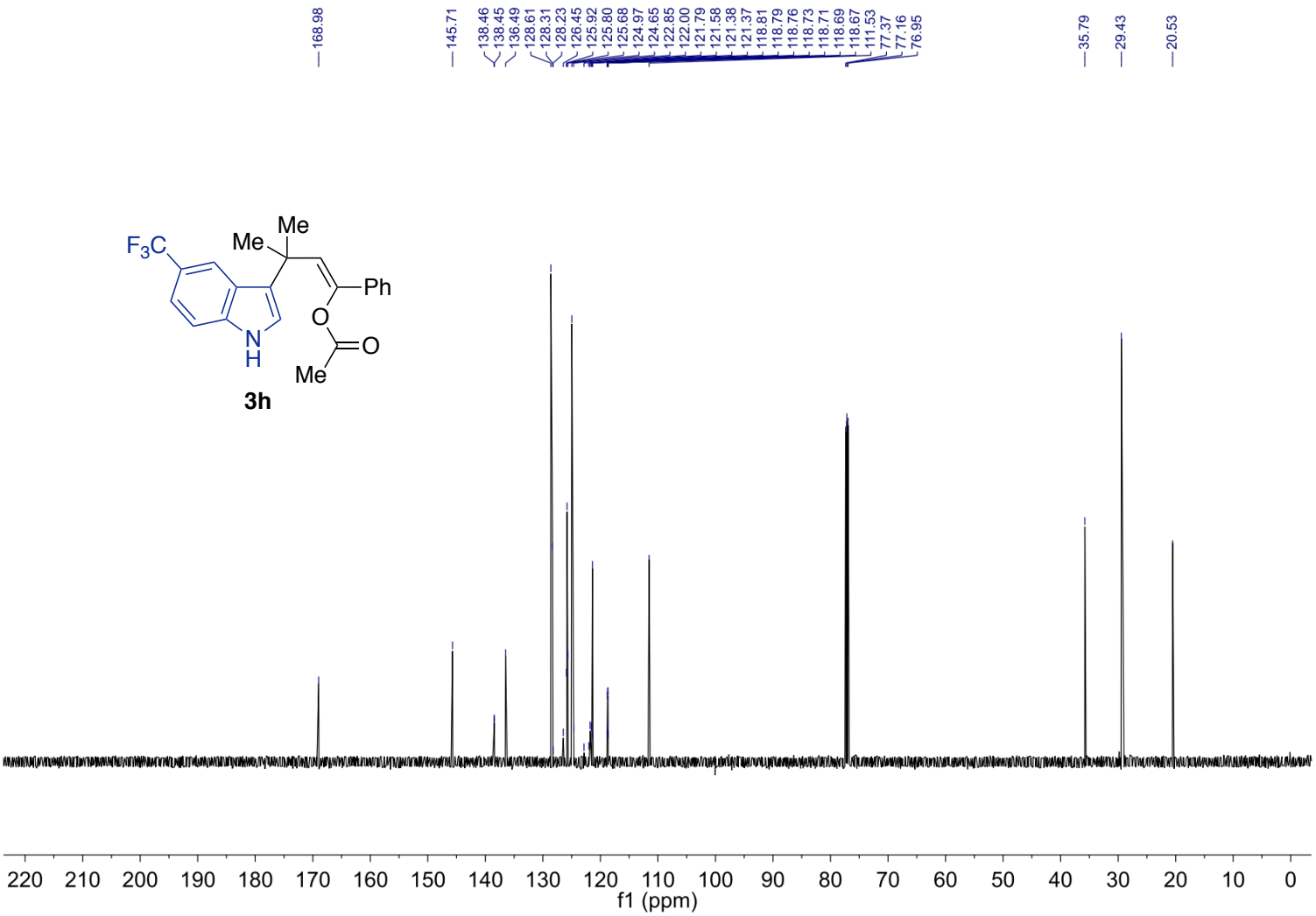
TSH-N6-83-6 1H

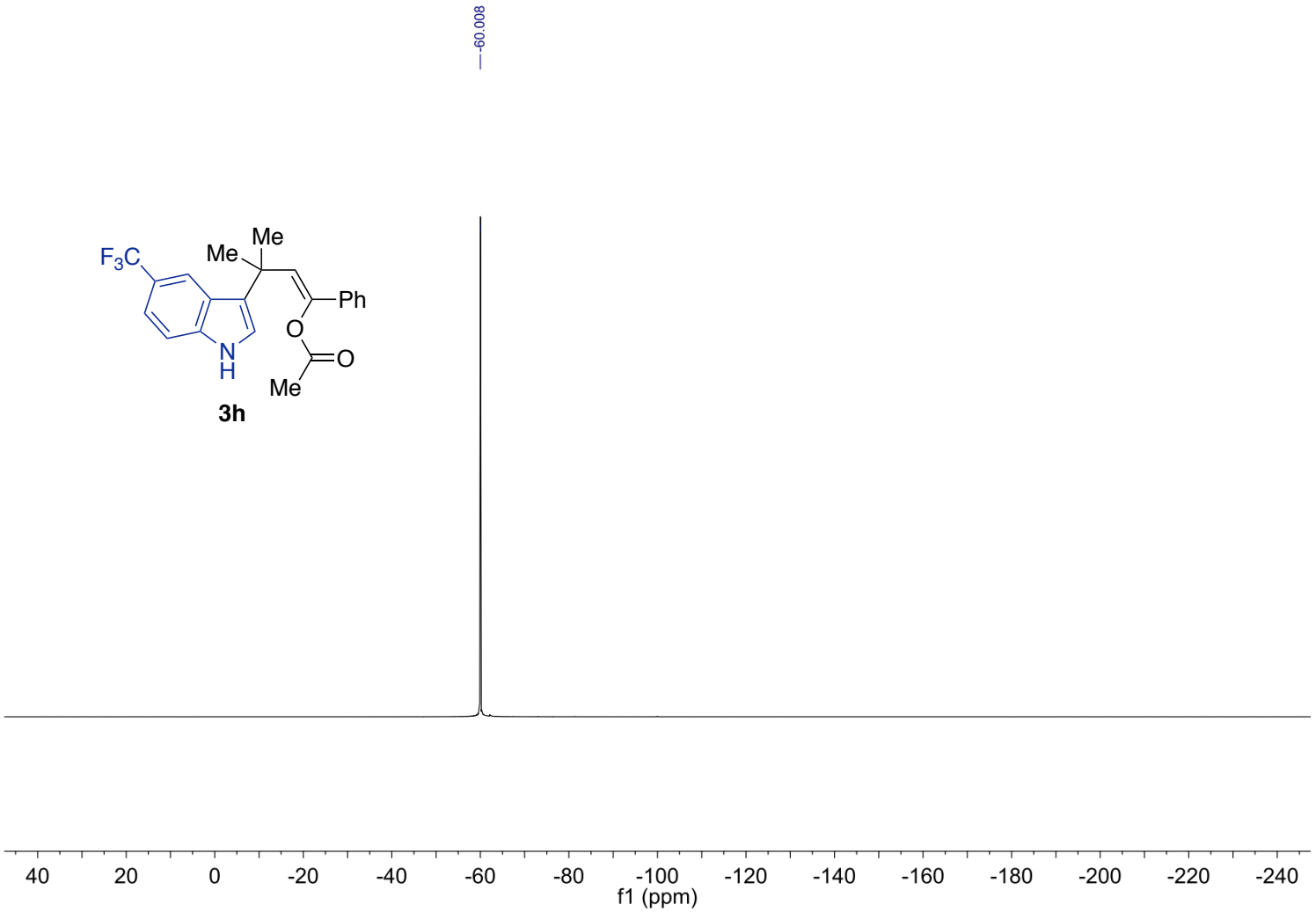


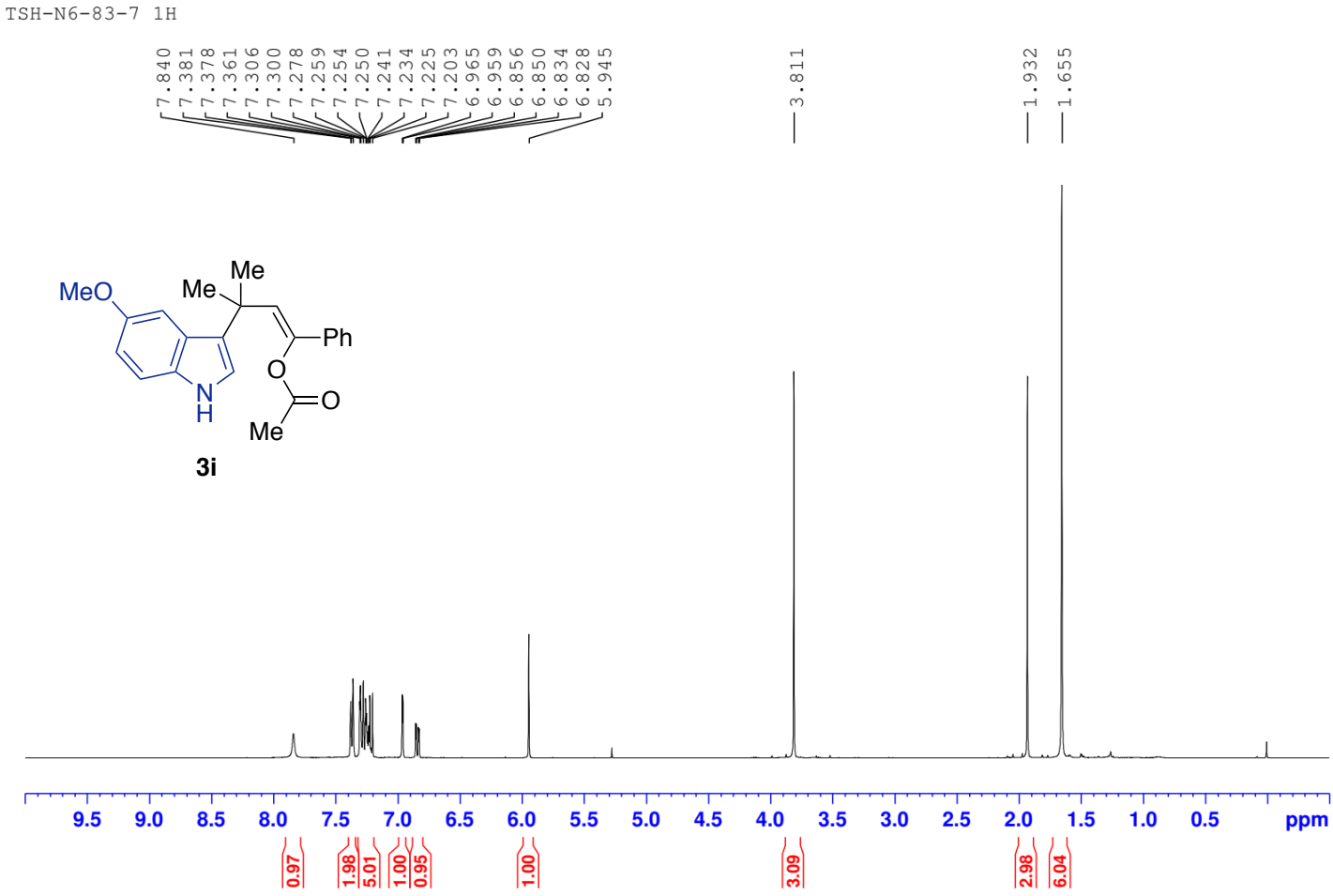
TSH-N6-83-6 13C



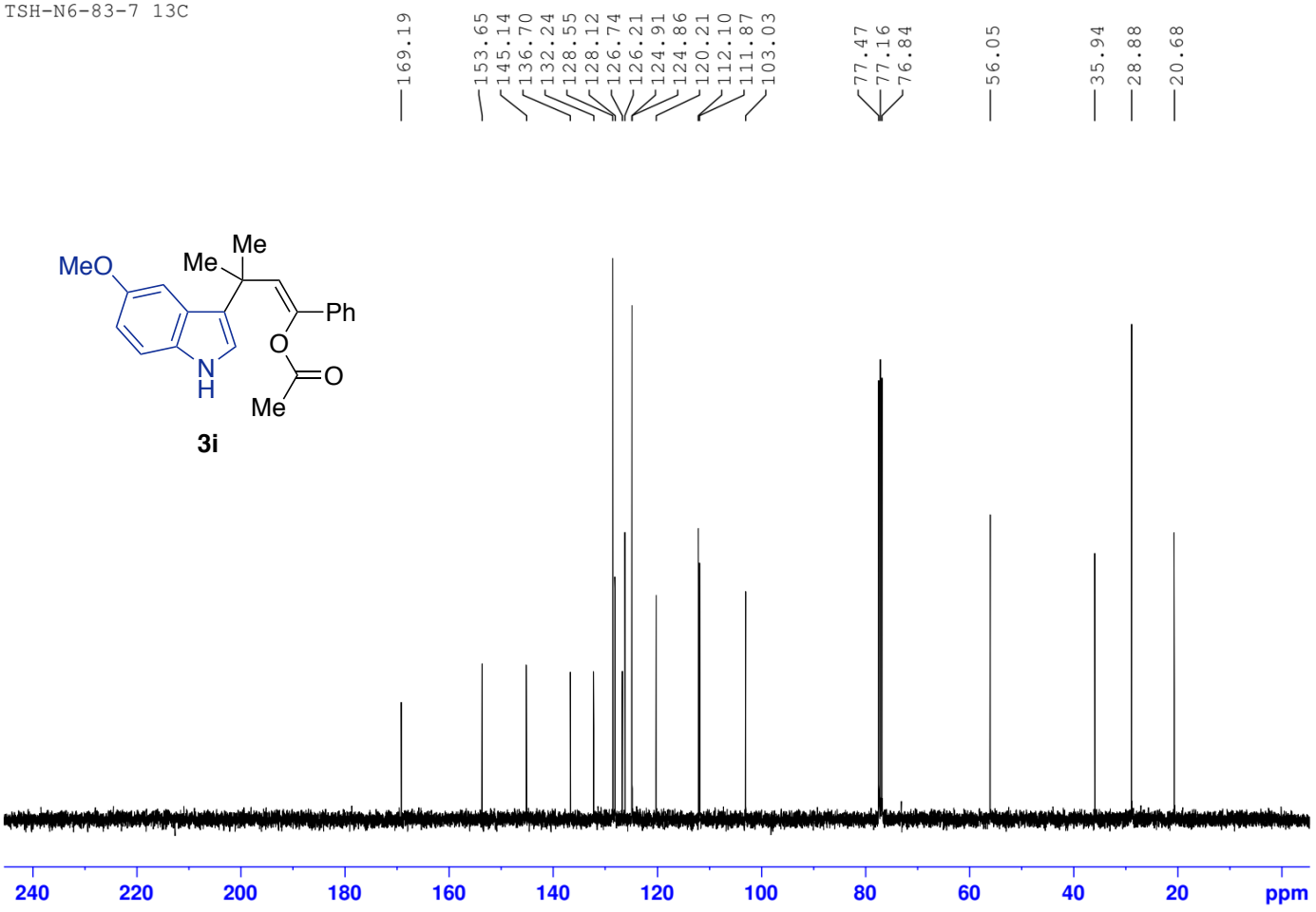

8.198
8.121
7.416
7.402
7.389
7.374
7.362
7.314
7.302
7.289
7.271
7.260
7.247
7.094
7.091
5.948
1.860
1.684
F3C
Me
Me
Ph
O
O
N
H
Me
3h
0.97
1.00
4.10
2.04
1.18
1.00
1.00
2.99
6.00
f1 (ppm)


168.98
145.71
138.46
138.45
136.49
128.61
128.31
128.23
126.45
125.92
125.80
125.68
124.97
124.65
122.85
122.00
121.79
121.58
121.38
121.37
118.81
118.79
118.76
118.73
118.71
118.69
118.67
111.53
77.37
77.16
76.95
35.79
29.43
20.53
F3C
Me
Me
Ph
O
O
N
H
Me
3h
f1 (ppm)

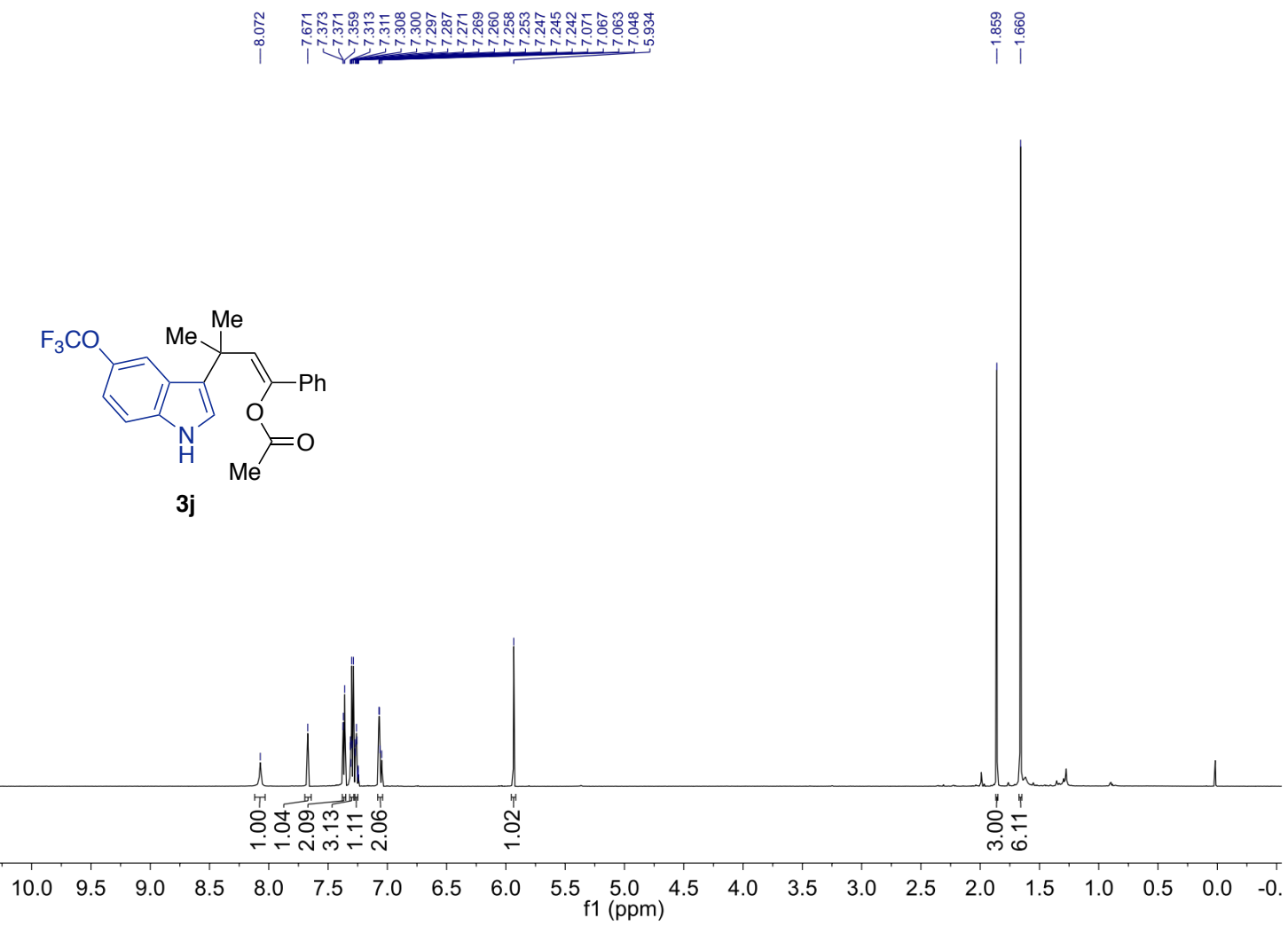

-60.008
F3C
Me
Me
Ph
O
O
N
H
Me
3h
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
f1 (ppm)


TSH-N6-83-7 1H
7.840
7.381
7.378
7.361
7.306
7.300
7.278
7.259
7.254
7.250
7.241
7.234
7.225
7.203
6.965
6.959
6.856
6.850
6.834
6.828
5.945
3.811
1.932
1.655
MeO
Me
Me
Ph
O
O
N
H
Me
3i
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
0.97
1.98
5.01
1.00
0.95
1.00
3.09
2.98
6.04

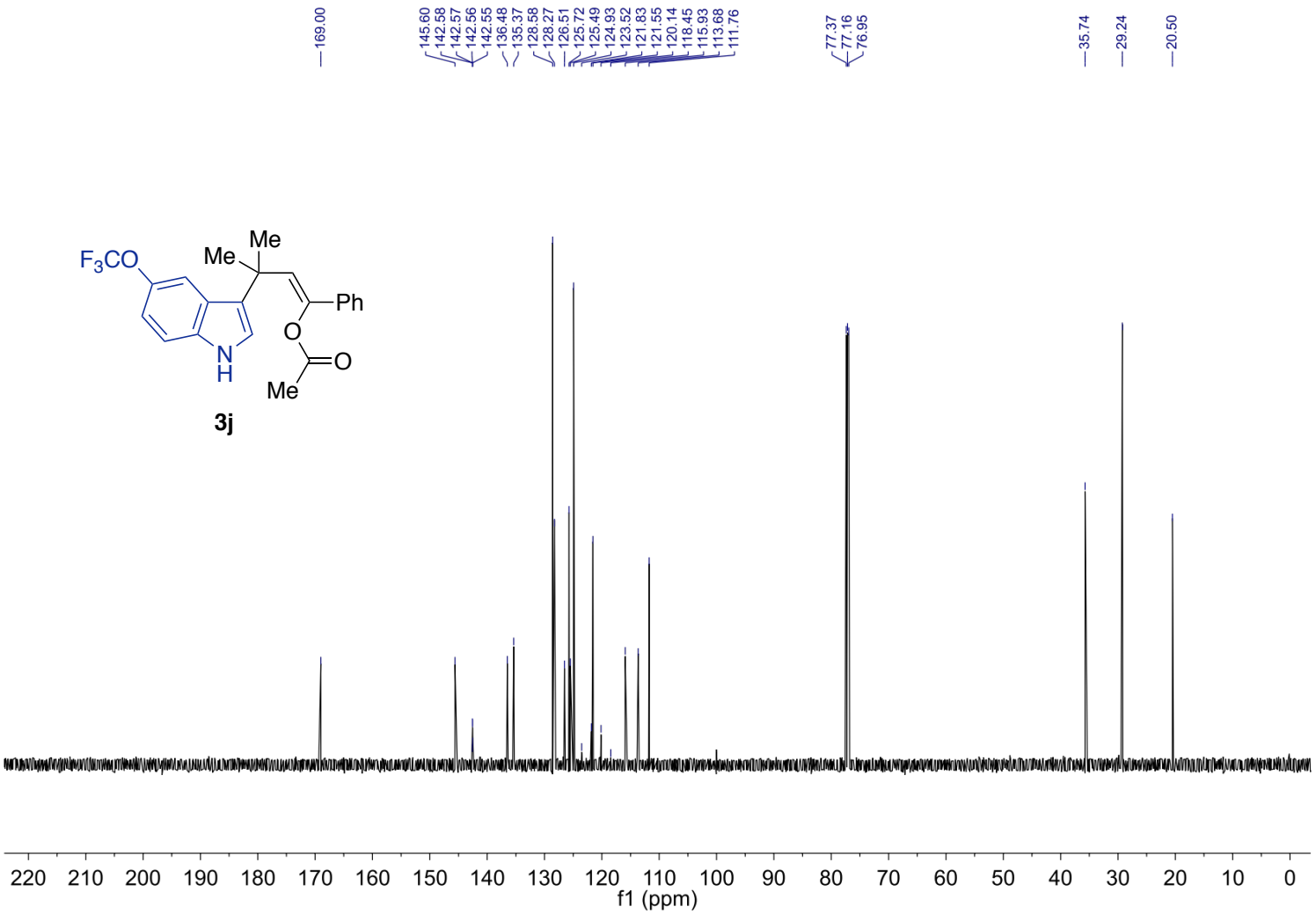
TSH-N6-83-7 13C

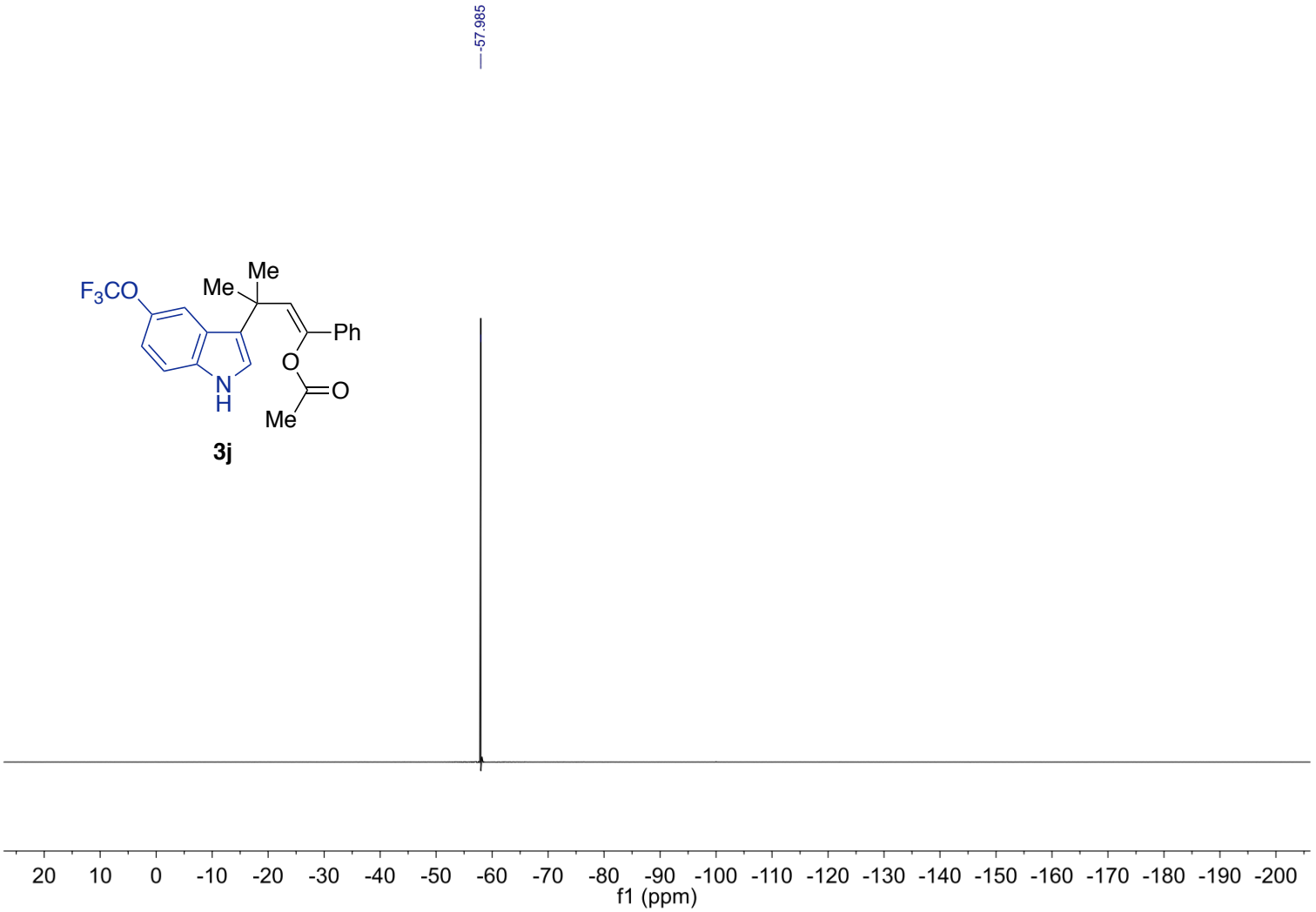


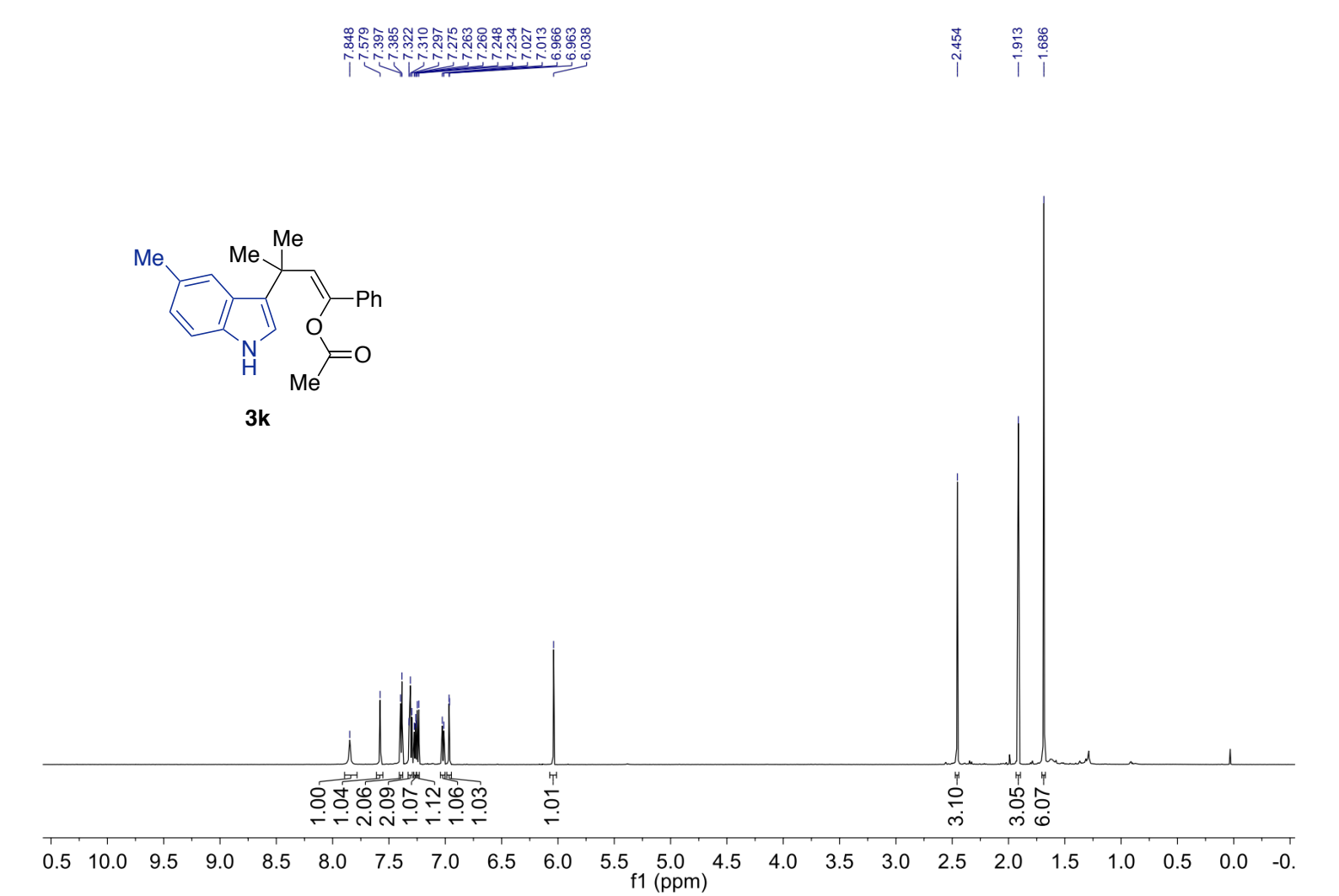
3i

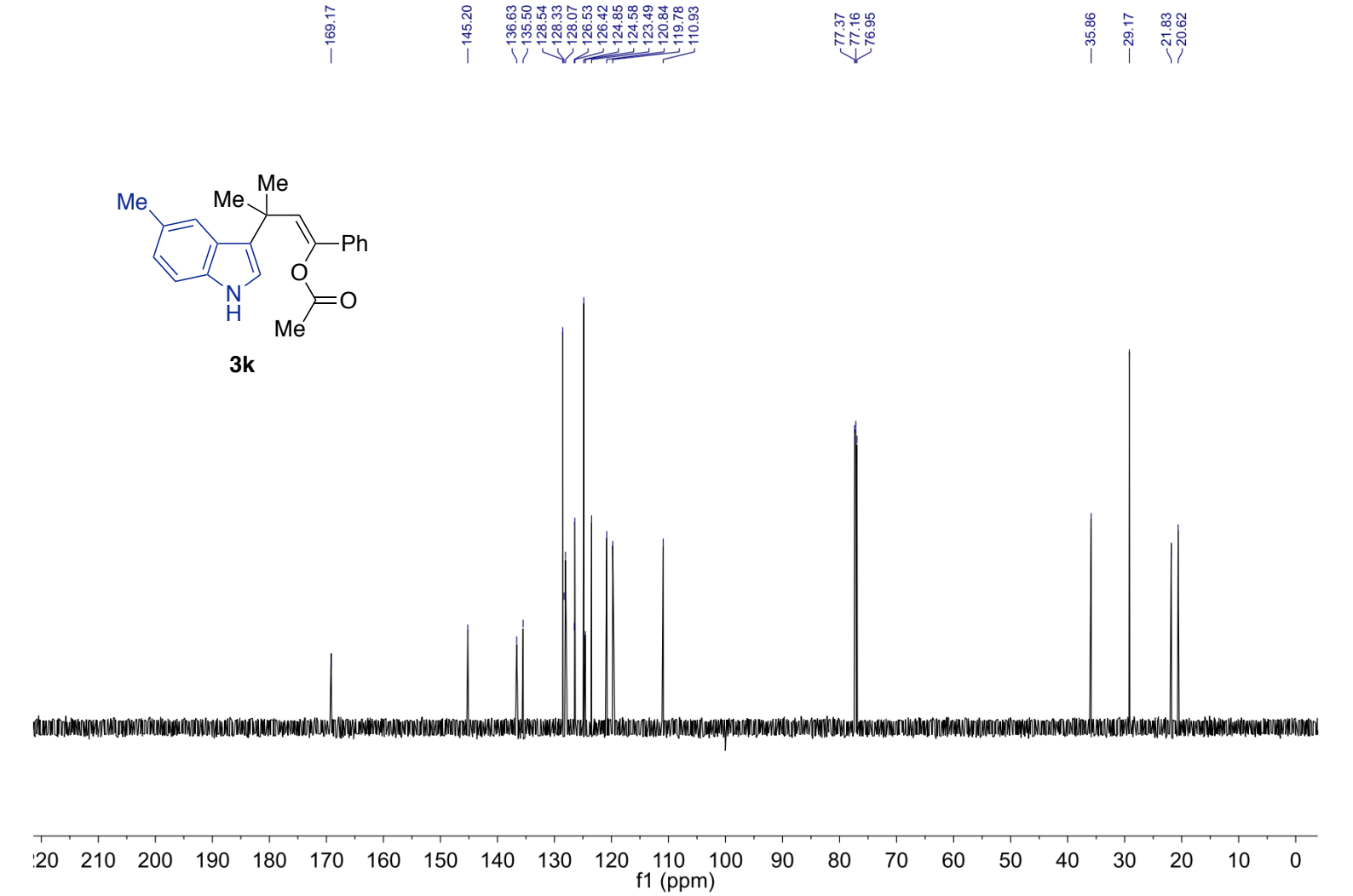


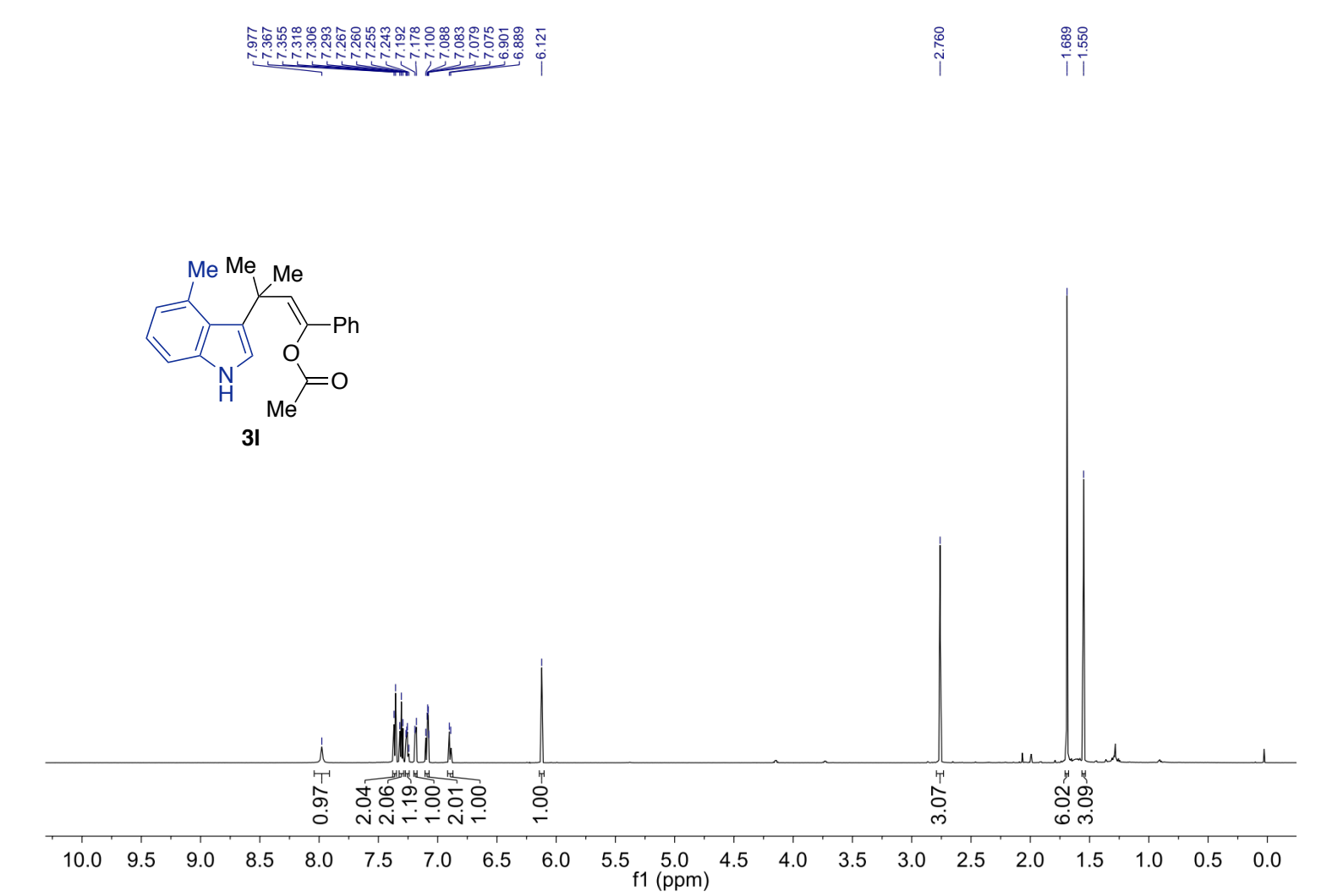
3j

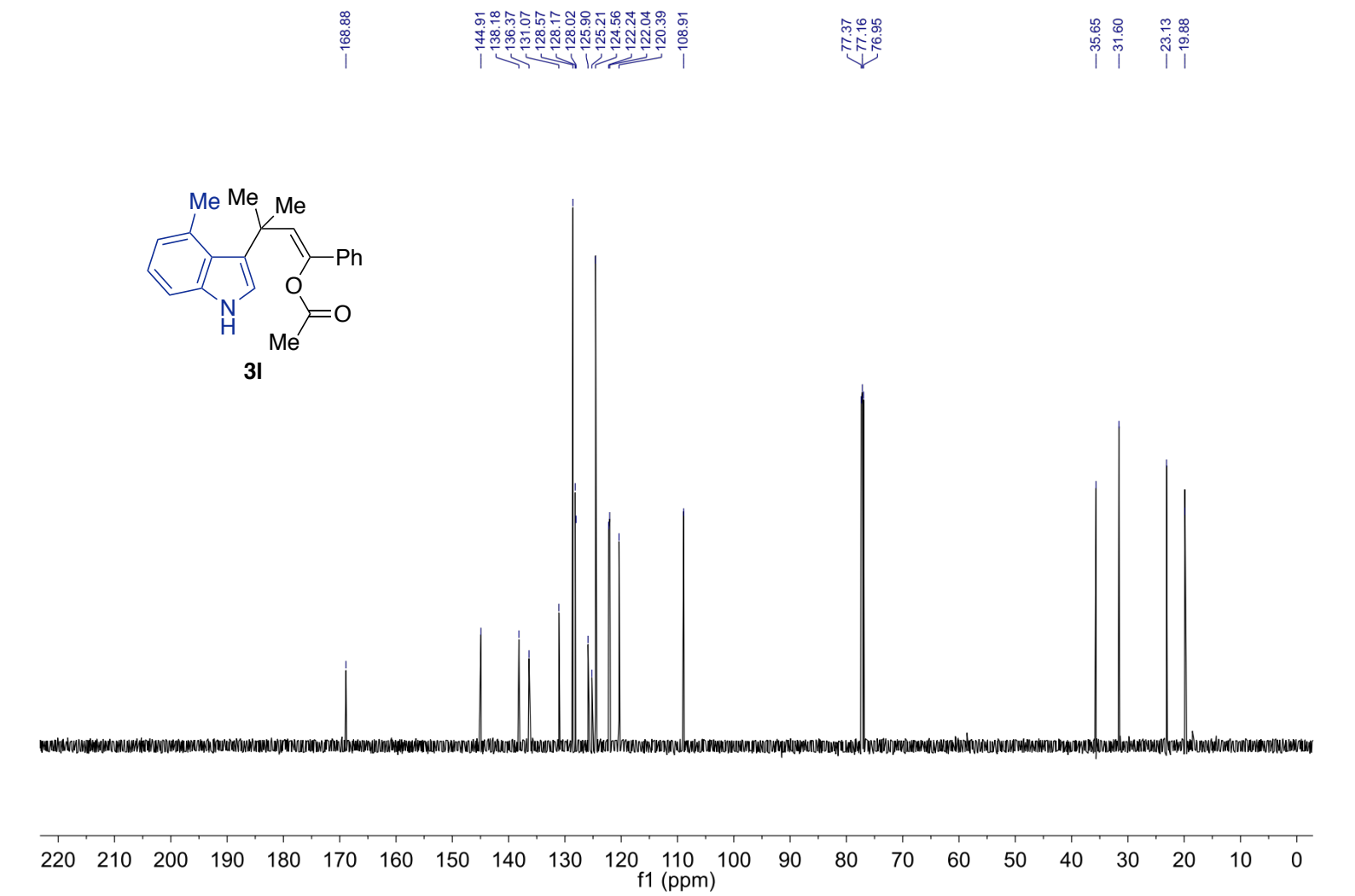

169.00
145.60
142.58
142.57
142.56
142.55
136.48
135.37
128.58
128.27
126.51
125.72
125.49
124.93
123.52
121.83
121.55
120.14
118.45
115.93
113.68
111.76
77.37
77.16
76.95
35.74
29.24
20.50
F3CO
Me
Me
Ph
O
O
N
H
Me
3j
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

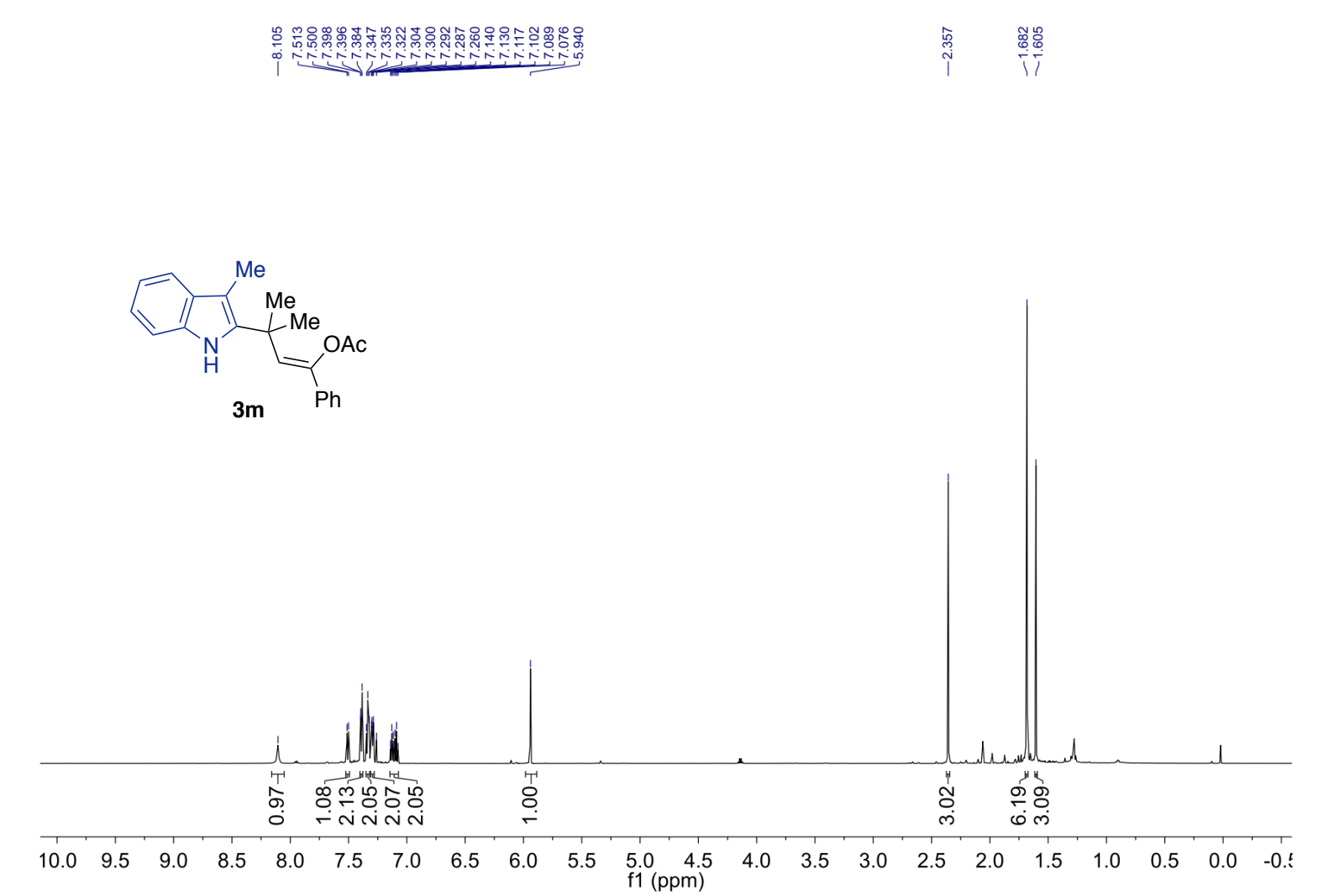

-57.985
F3CO
Me
Me
Ph
O
O
N
H
Me
3j
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

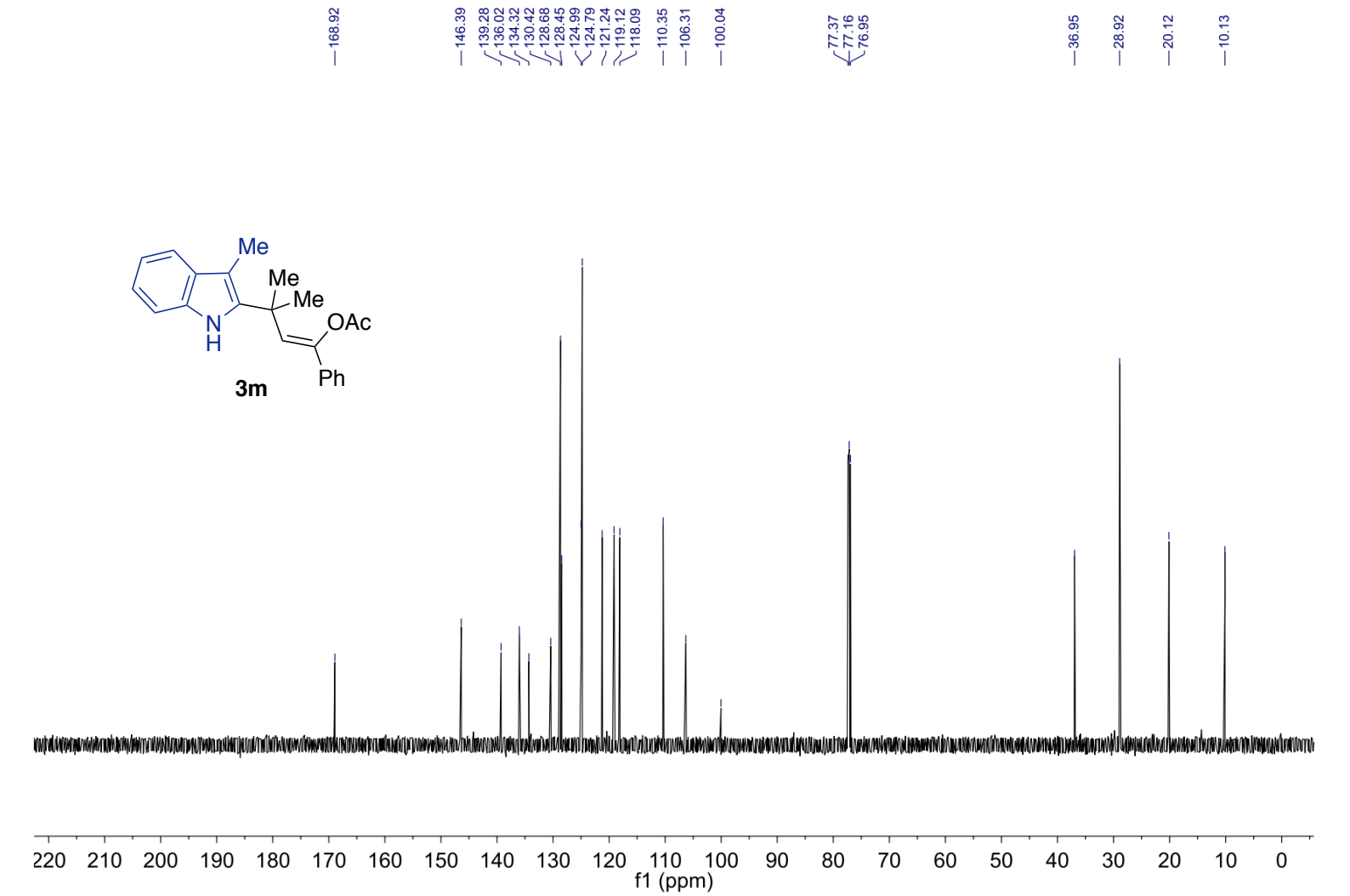

7.848
7.579
7.397
7.385
7.322
7.310
7.297
7.275
7.263
7.260
7.248
7.234
7.027
7.013
6.966
6.963
6.038
2.454
1.913
1.686
Me
Me
Me
Ph
O
O
N
H
Me
3k
1.00
1.04
2.06
2.09
1.07
1.12
1.06
1.03
1.01
3.10
3.05
6.07
f1 (ppm)

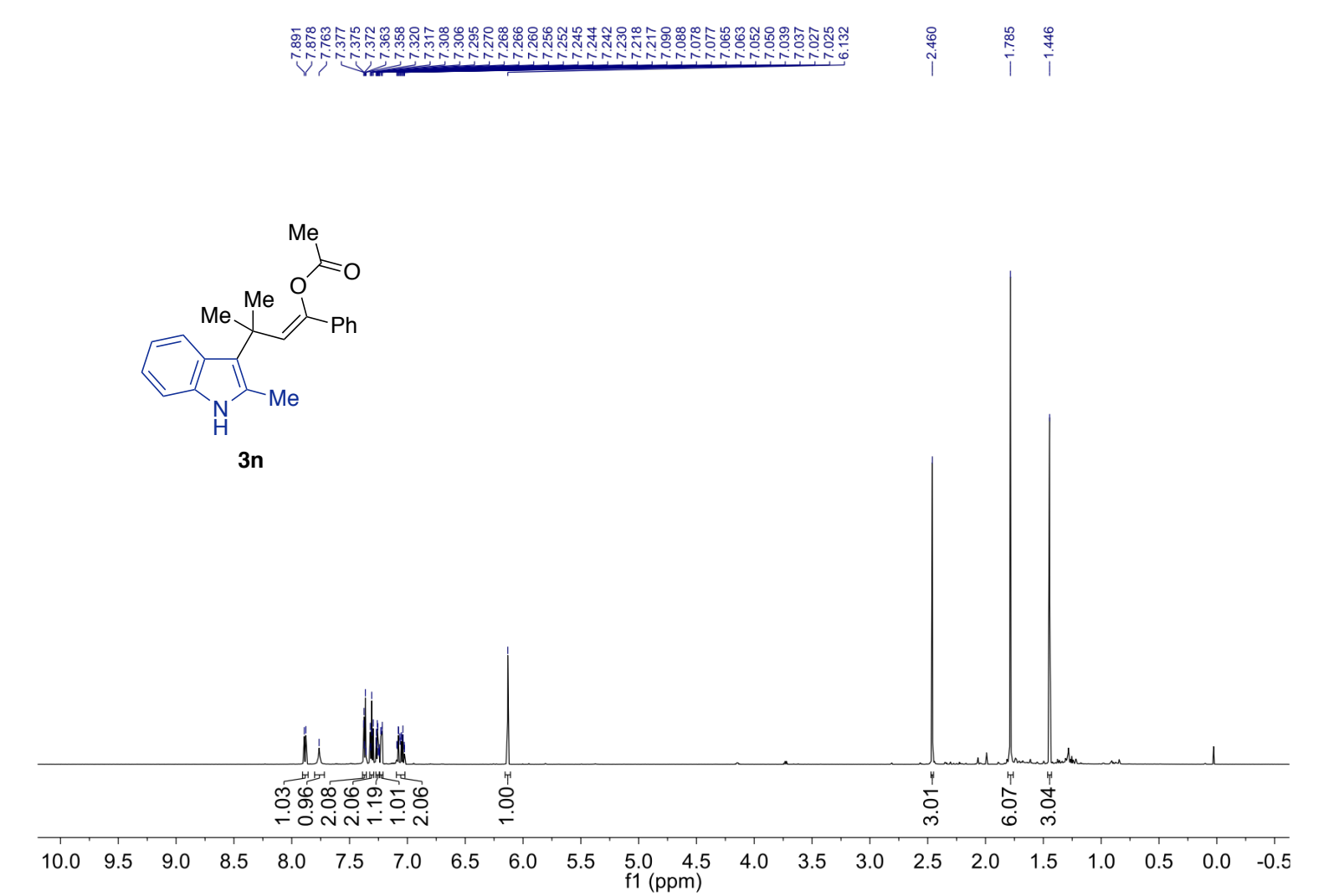

169.17
145.20
136.63
135.50
128.54
128.33
128.07
126.53
126.42
124.85
124.58
123.49
120.84
119.78
110.93
77.37
77.16
76.95
35.86
29.17
21.83
20.62
Me
Me
Me
Ph
O
O
N
H
Me
3k
f1 (ppm)

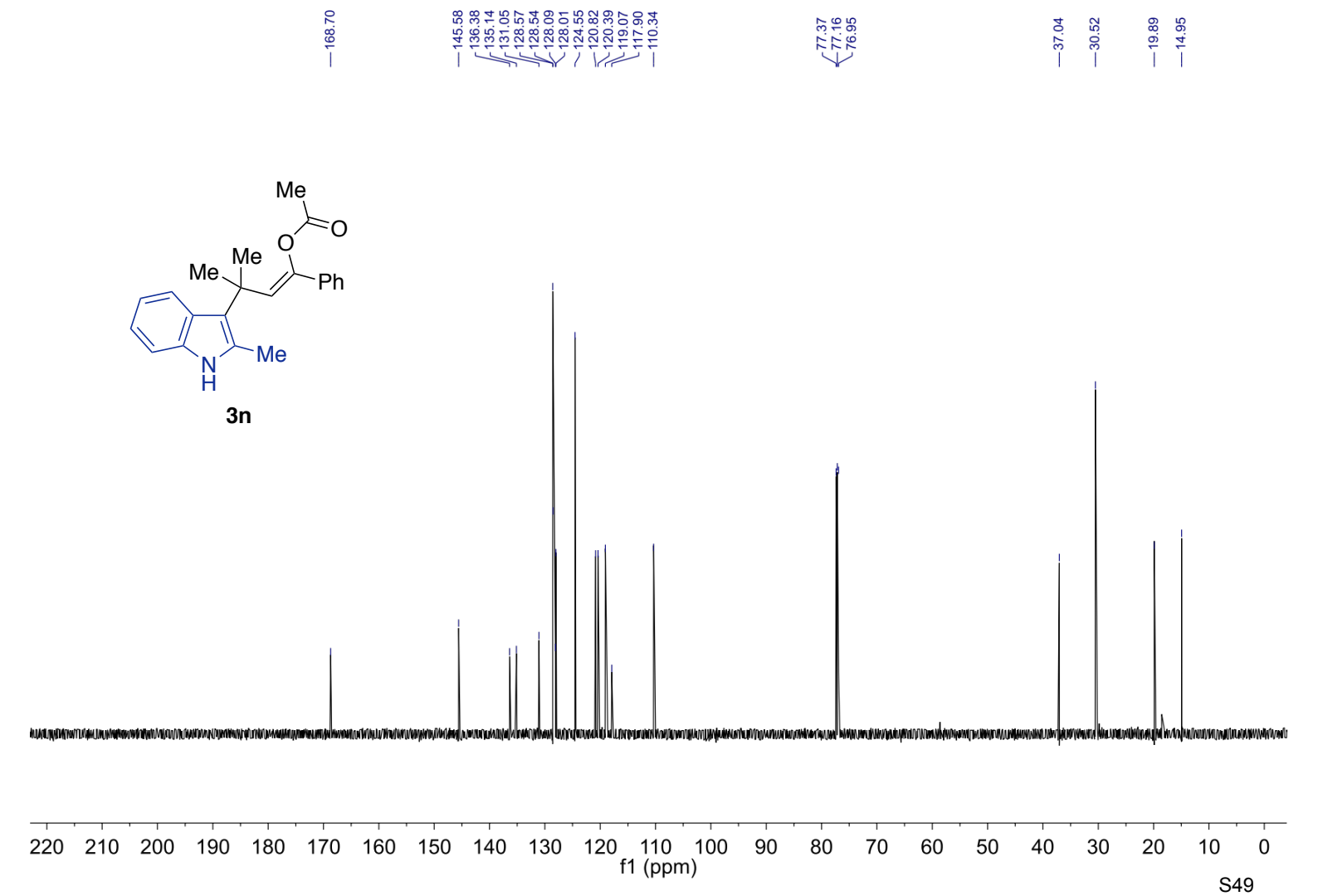

7.977
7.367
7.355
7.318
7.306
7.293
7.267
7.260
7.255
7.243
7.192
7.178
7.100
7.088
7.083
7.079
7.075
6.901
6.889
6.121
2.760
1.689
1.550
Me
Me
Me
Ph
O
O
N
H
Me
3l
0.97
2.04
2.06
1.19
1.00
2.01
1.00
1.00
3.07
6.02
3.09
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


168.88
144.91
138.18
136.37
131.07
128.57
128.17
128.02
125.90
125.21
124.56
122.24
122.04
120.39
108.91
77.37
77.16
76.95
35.65
31.60
23.13
19.88
Me
Me
Me
Ph
O
O
N
H
Me
3l
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

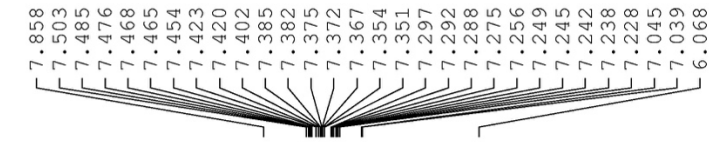

8.105
7.513
7.500
7.398
7.396
7.384
7.347
7.335
7.322
7.304
7.300
7.292
7.287
7.260
7.140
7.130
7.117
7.102
7.089
7.076
5.940
2.357
1.682
1.605
Me
Me
Me
OAc
N
H
Ph
3m
0.97
1.08
2.13
2.05
2.07
2.05
1.00
3.02
6.19
3.09
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

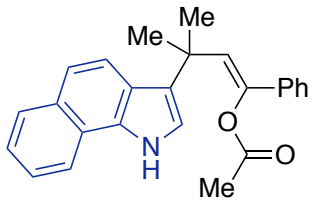

168.92
146.39
139.28
136.02
134.32
130.42
128.68
128.45
124.99
124.79
121.24
119.12
118.09
110.35
106.31
100.04
77.37
77.16
76.95
36.95
28.92
20.12
10.13
Me
Me
Me
OAc
N
H
Ph
3m
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.891
7.878
7.763
7.377
7.375
7.372
7.363
7.358
7.320
7.317
7.308
7.306
7.295
7.270
7.268
7.266
7.260
7.256
7.252
7.245
7.244
7.242
7.230
7.218
7.217
7.090
7.088
7.078
7.077
7.065
7.063
7.052
7.050
7.039
7.037
7.027
7.025
6.132
2.460
1.785
1.446
Me
O
O
Me
Me
Ph
Me
N
H
3n
1.03
0.96
2.08
2.06
1.19
1.01
2.06
1.00
3.01
6.07
3.04
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


168.70
145.58
136.38
135.14
131.05
128.57
128.54
128.09
128.01
124.55
120.82
120.39
119.07
117.90
110.34
77.37
77.16
76.95
37.04
30.52
19.89
14.95
Me
O
O
Me
Me
Ph
Me
N
H
3n
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

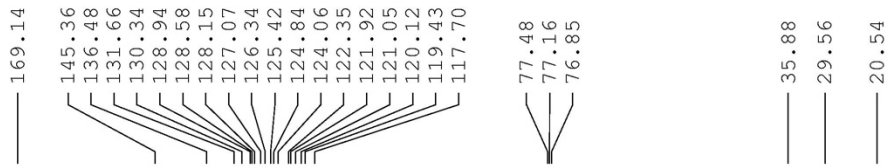
TSH-N6-83-4 1H

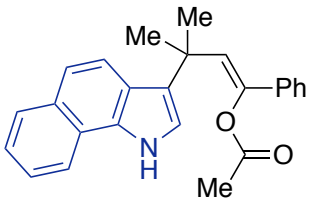




3o

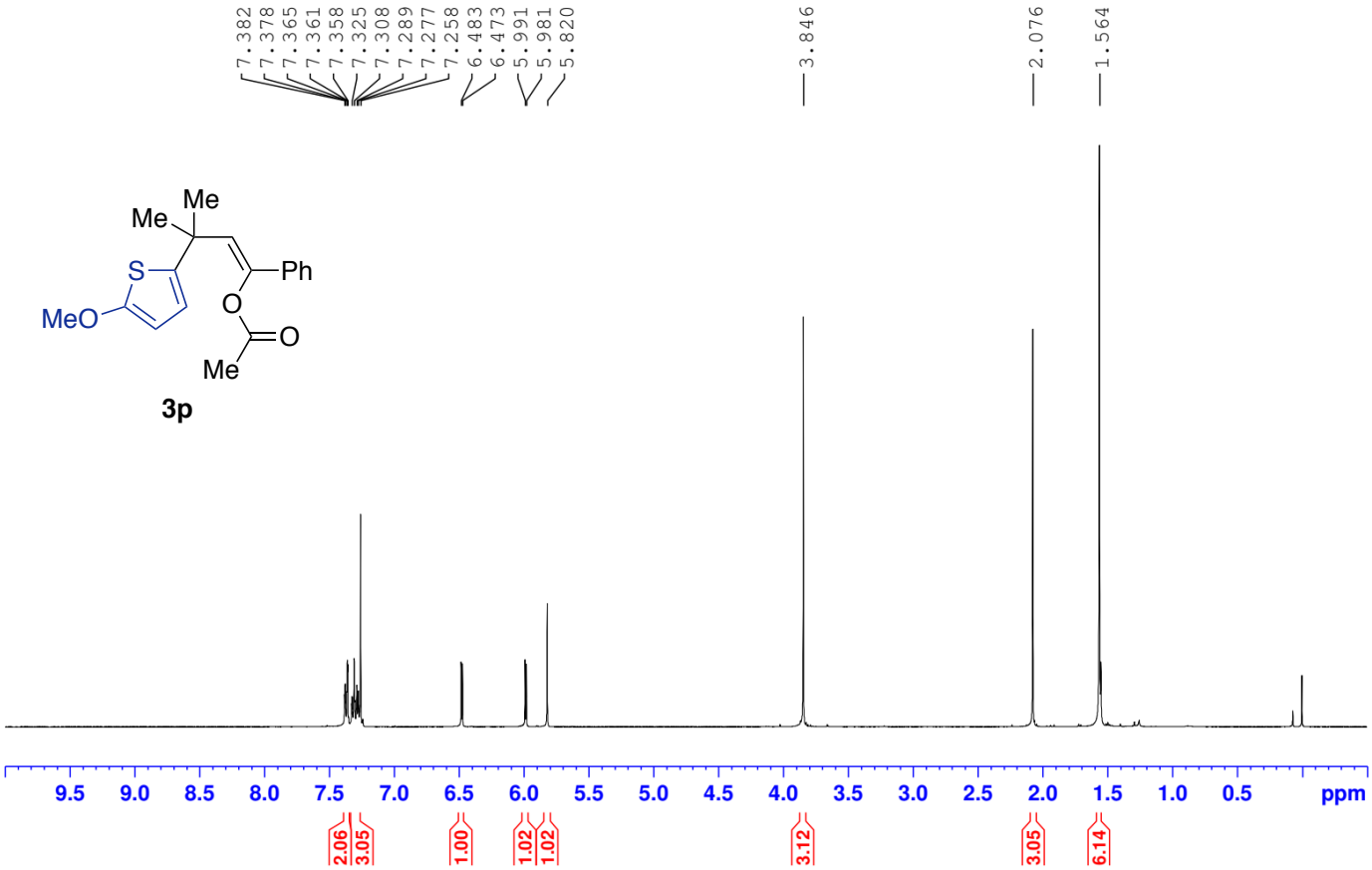
TSH-N6-83-4 13C



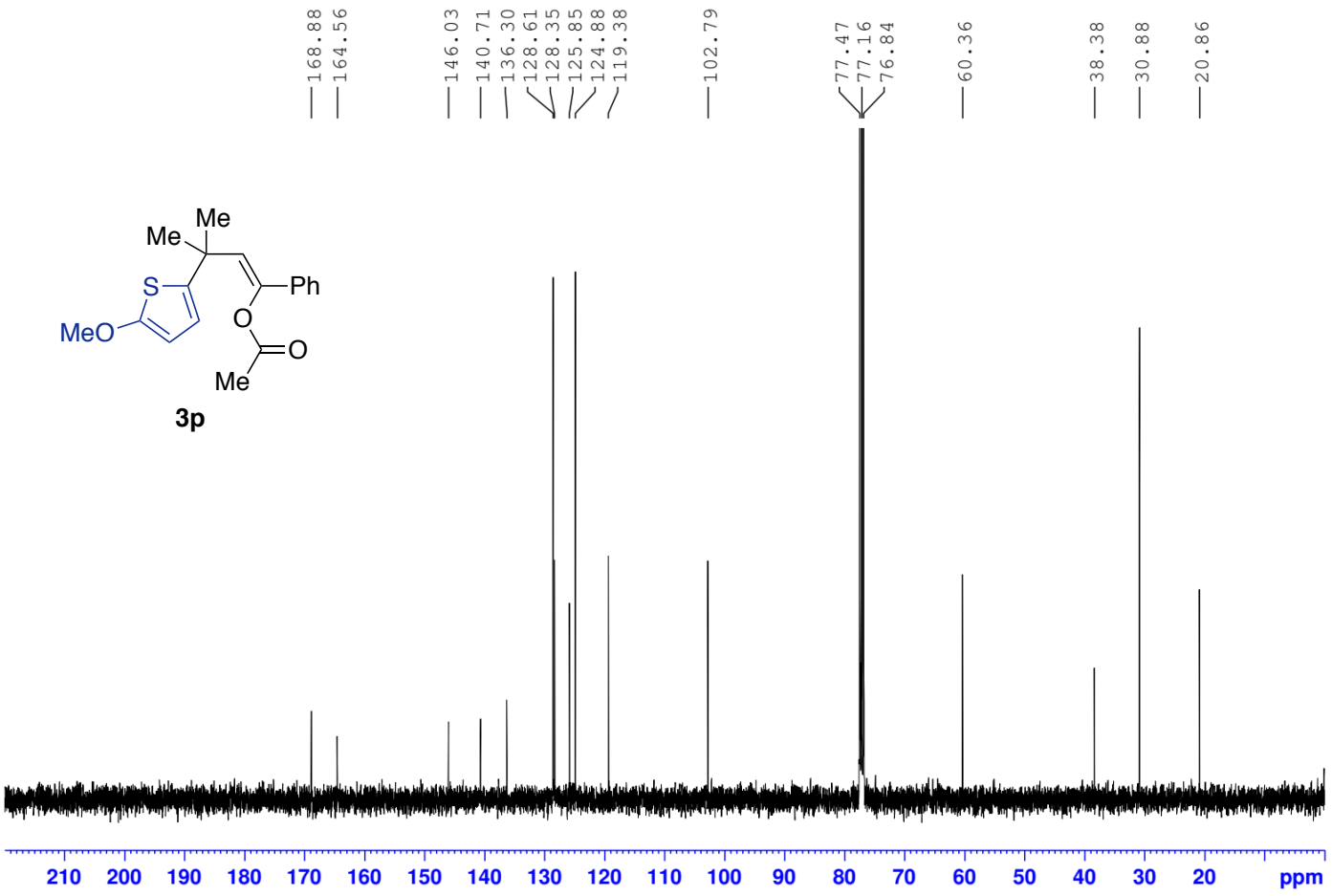


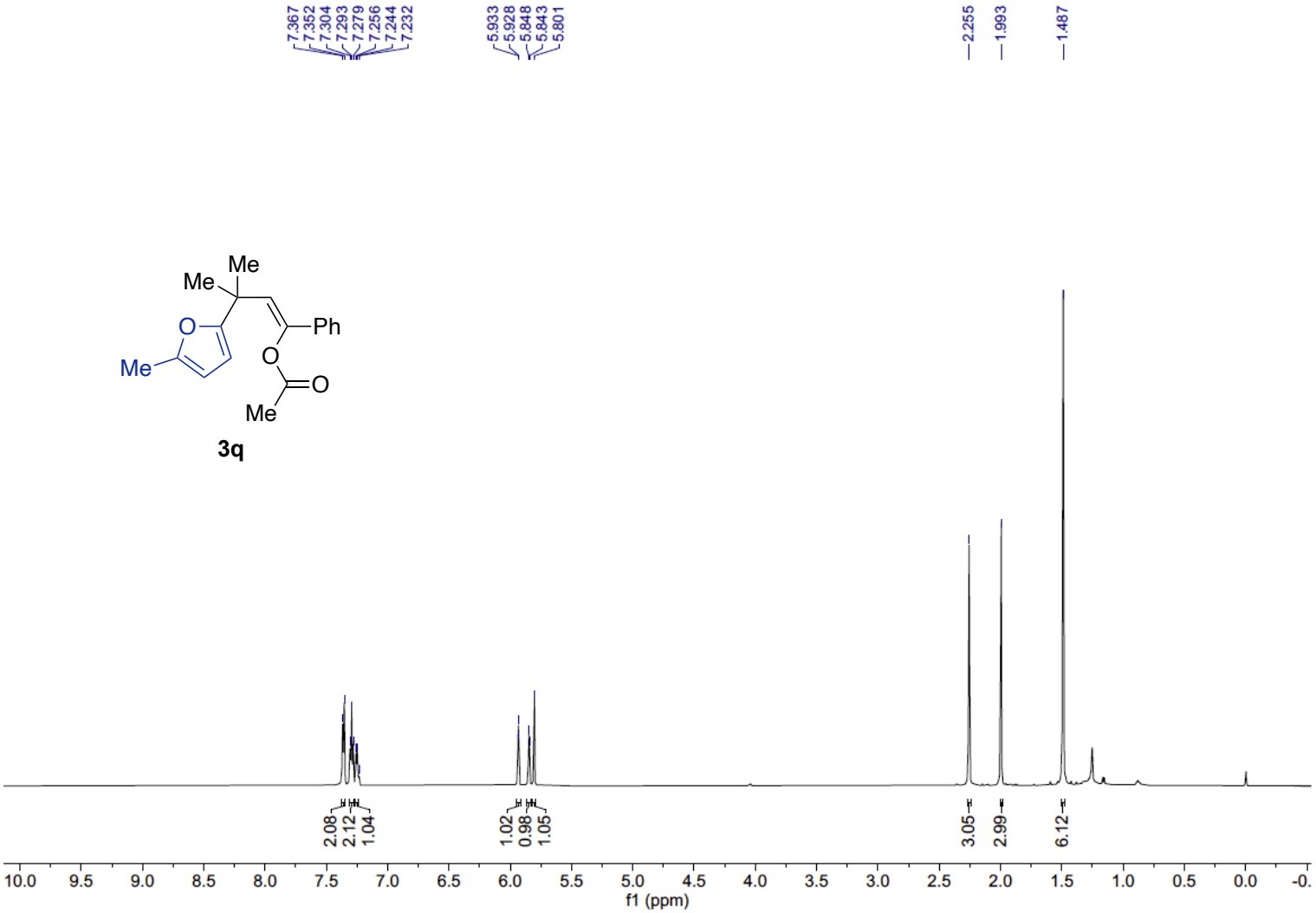
3o

TSH-N6-89-2 1H

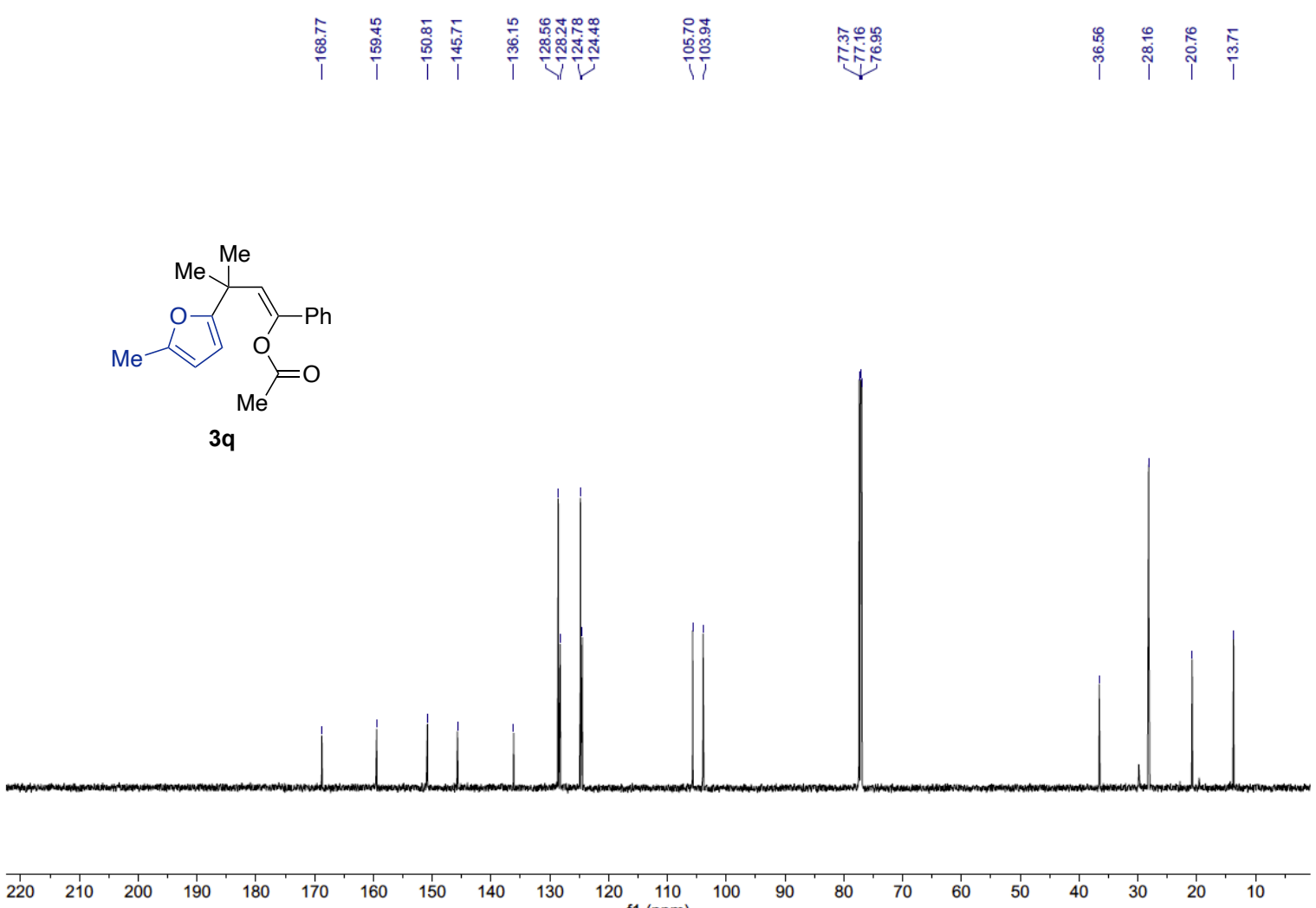


TSH-N6-89-2 13C

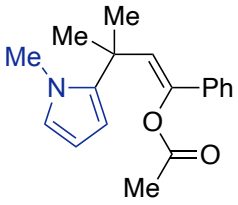



7.367
7.352
7.304
7.293
7.279
7.256
7.244
7.232
5.933
5.928
5.848
5.843
5.801
2.255
1.993
1.487
Me
Me
O
Ph
Me
O
O
Me
2.08
2.12
1.04
1.02
0.98
1.05
3.05
2.99
6.12
f1 (ppm)

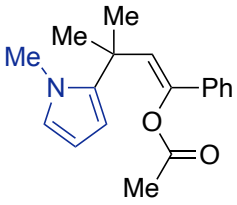
3q


168.77
159.45
150.81
145.71
136.15
128.56
128.24
124.78
124.48
105.70
103.94
77.37
77.16
76.95
36.56
28.16
20.76
13.71
Me
Me
O
Ph
Me
O
O
Me
f1 (ppm)

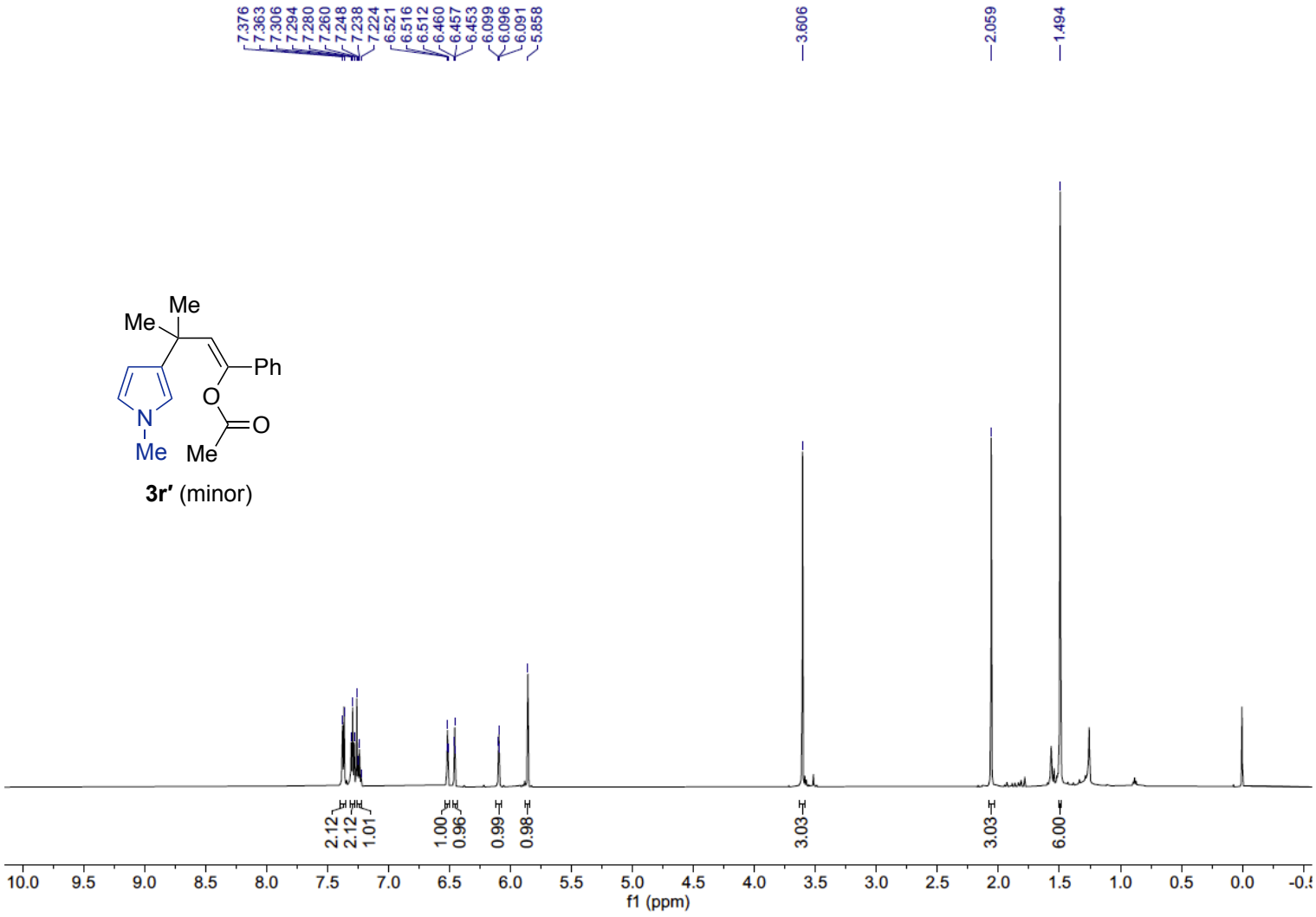
3q



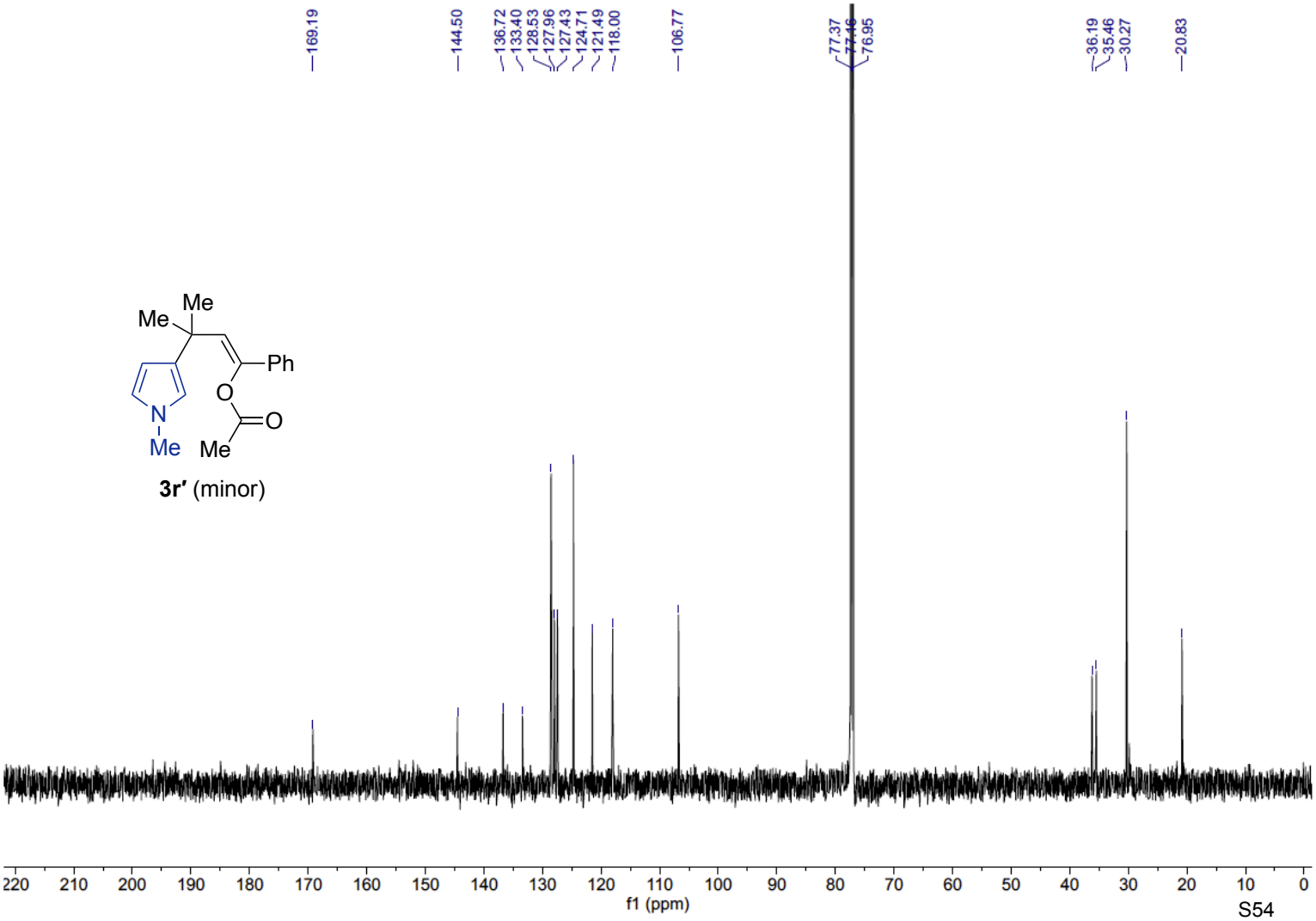
3r (major)



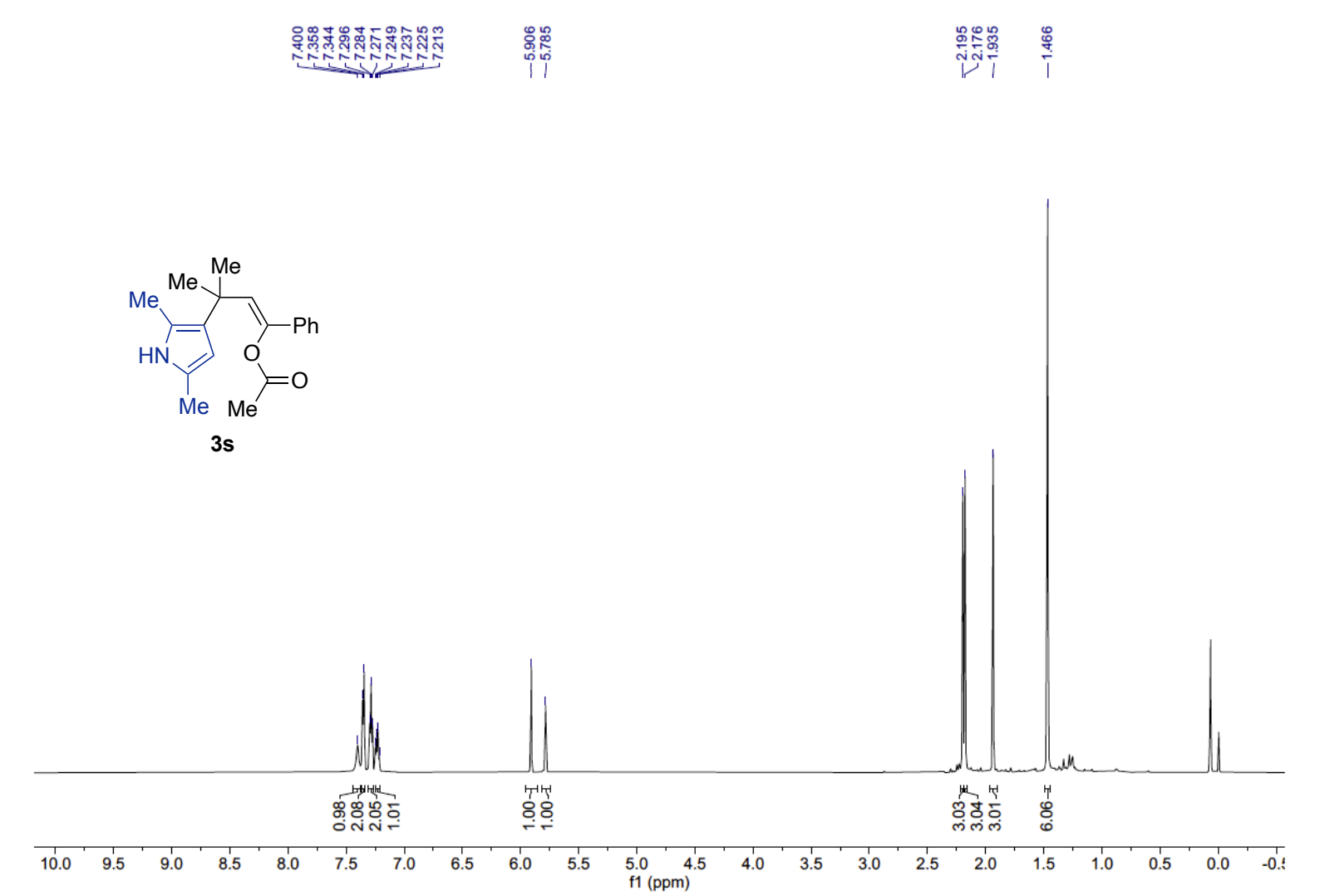
3r (major)



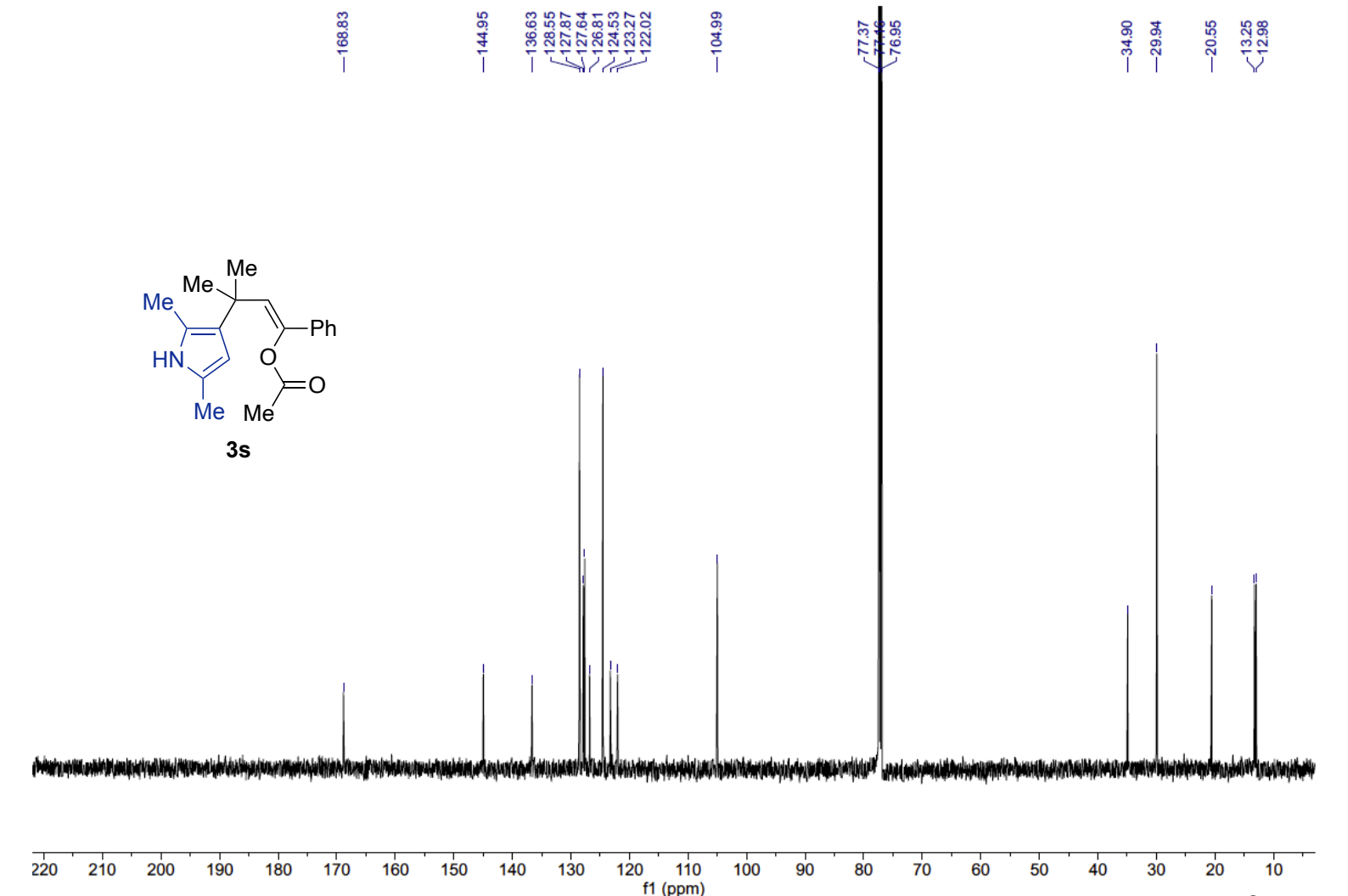
3r′ (minor)



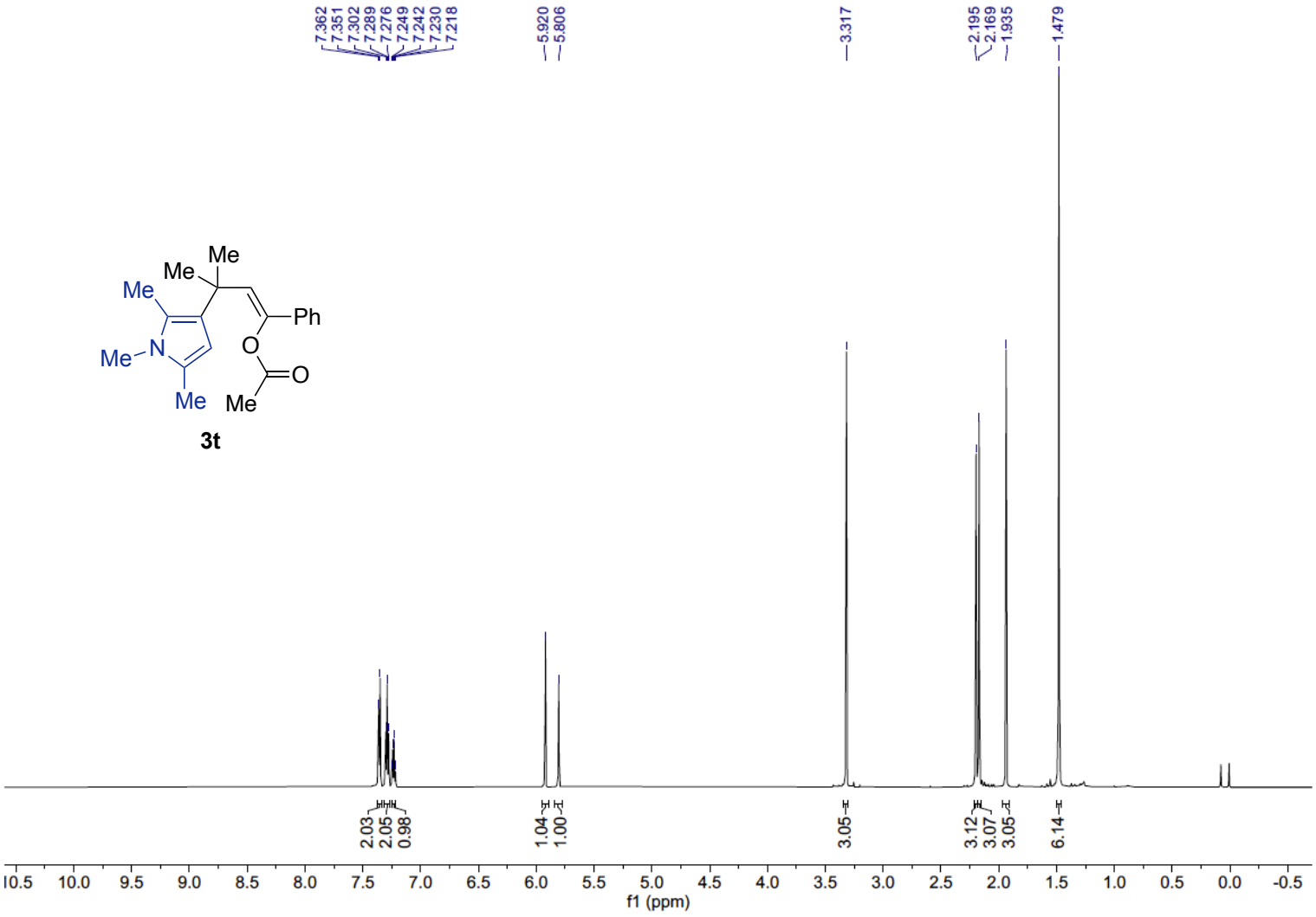
3r′ (minor)


7.400
7.358
7.344
7.296
7.284
7.271
7.249
7.237
7.225
7.213
5.906
5.785
2.195
2.176
1.935
1.466
Me
Me
Me
HN
Me
Ph
O
O
Me
0.98
2.08
2.05
1.01
1.00
1.00
3.03
3.04
3.01
6.06
f1 (ppm)

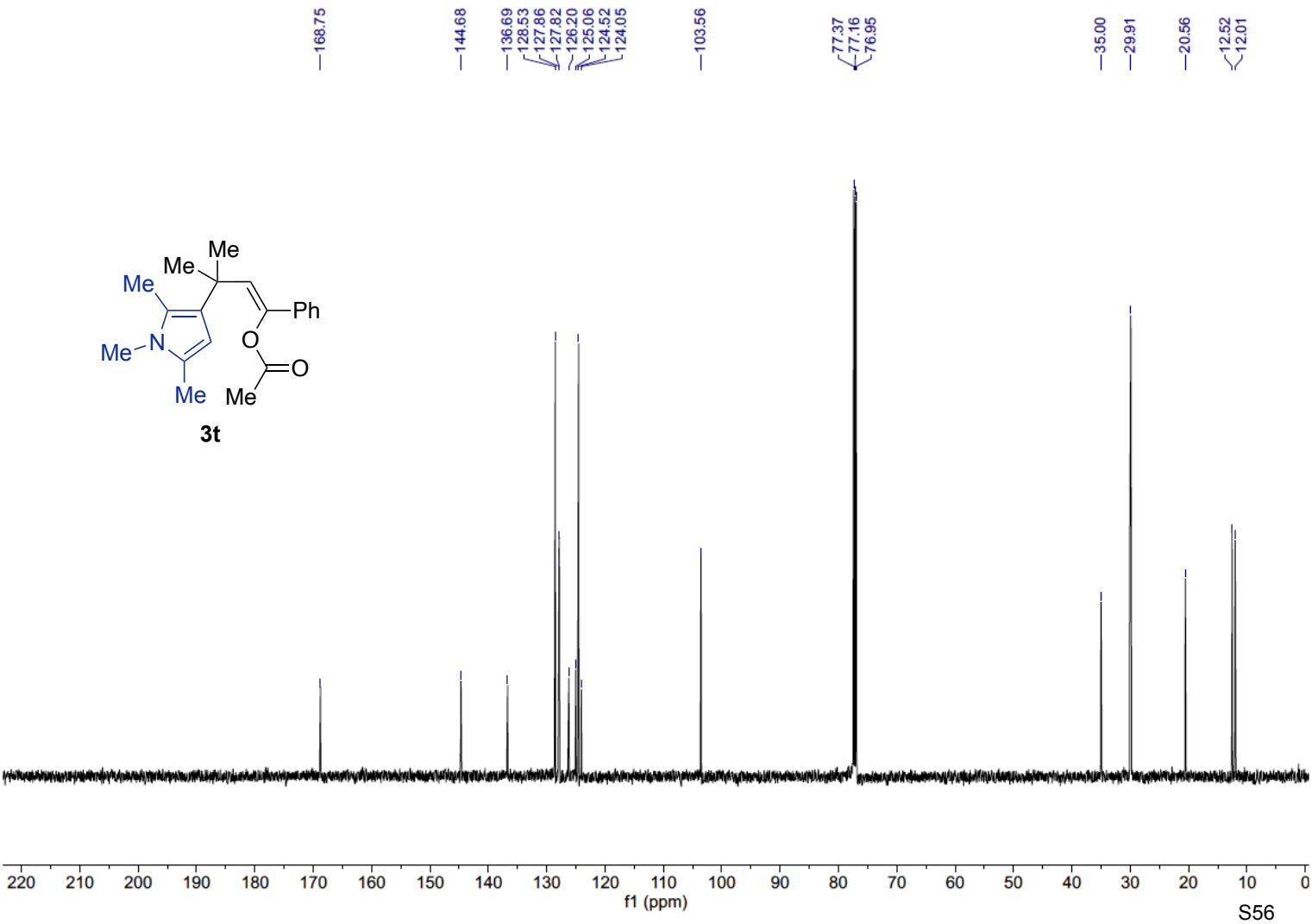
3s


168.83
144.95
136.63
128.55
127.87
127.64
126.81
124.53
123.27
122.02
104.99
77.37
77.16
76.95
34.90
29.94
20.55
13.25
12.98
Me
Me
Me
HN
Me
Ph
O
O
Me
f1 (ppm)

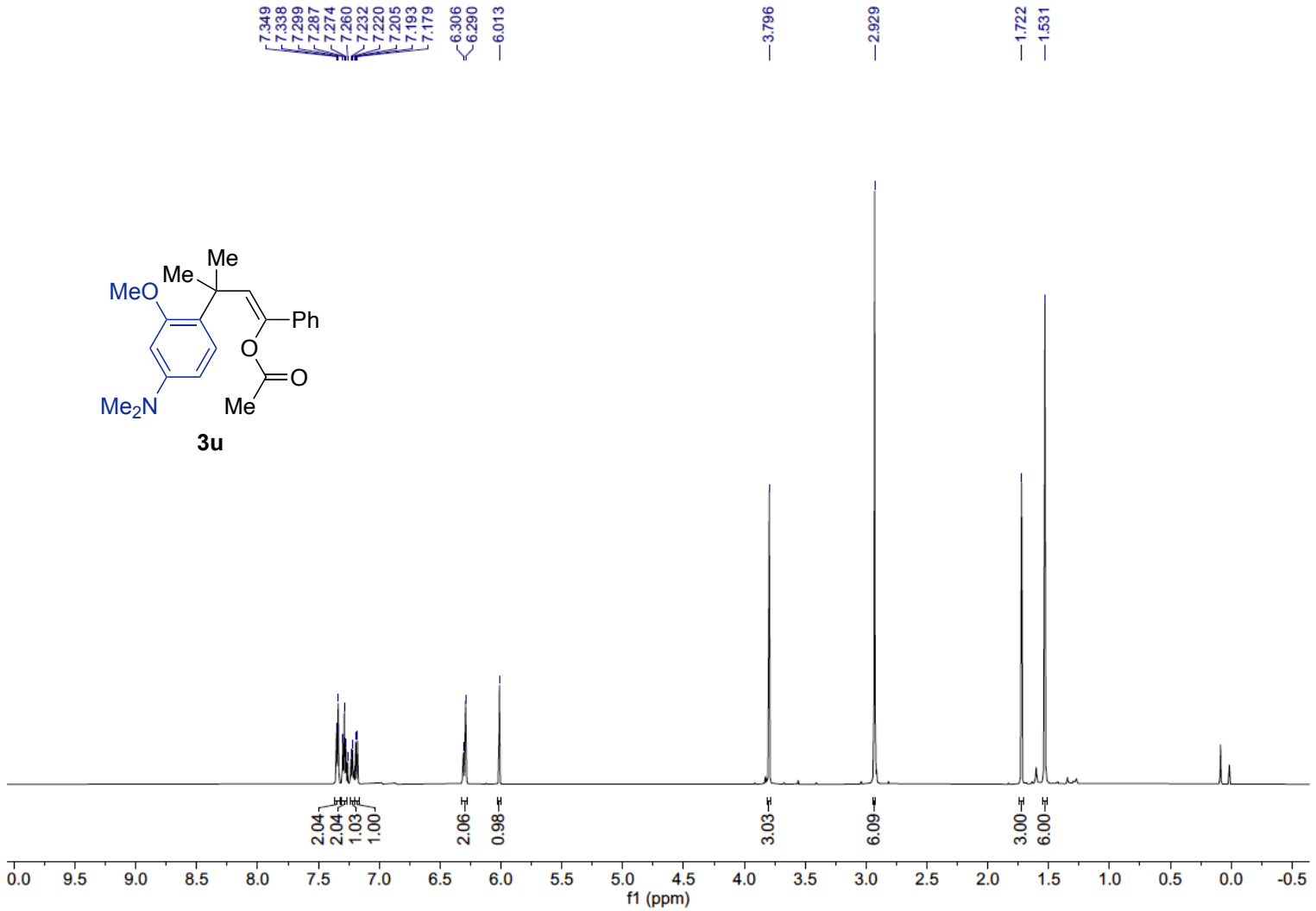
3s

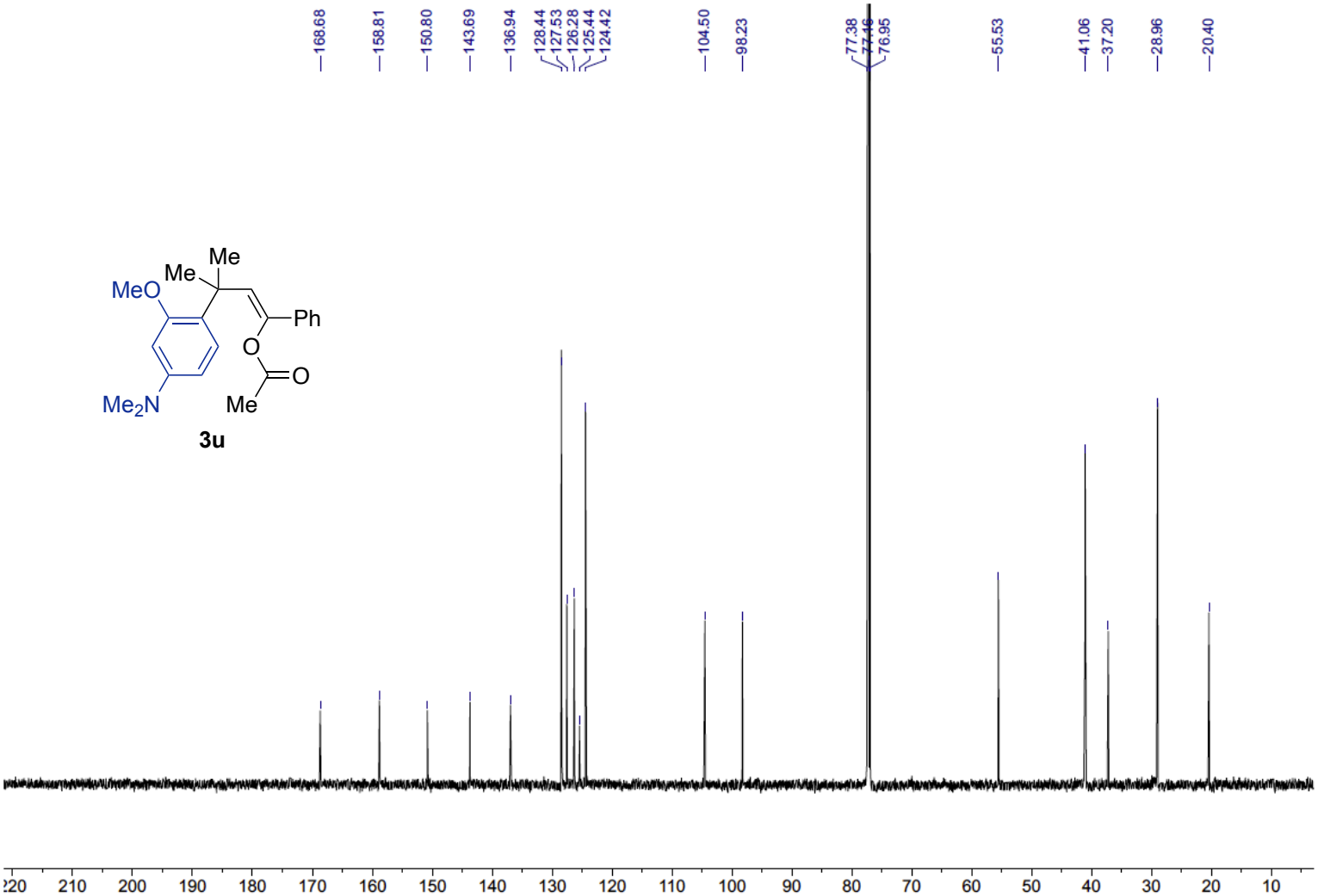

7.362
7.351
7.302
7.289
7.276
7.249
7.242
7.230
7.218
5.920
5.806
3.317
2.195
2.169
1.935
1.479
Me
Me
Me
Ph
Me
N
O
O
Me
Me
2.03
2.05
0.98
1.04
1.00
3.05
3.12
3.07
3.05
6.14
f1 (ppm)

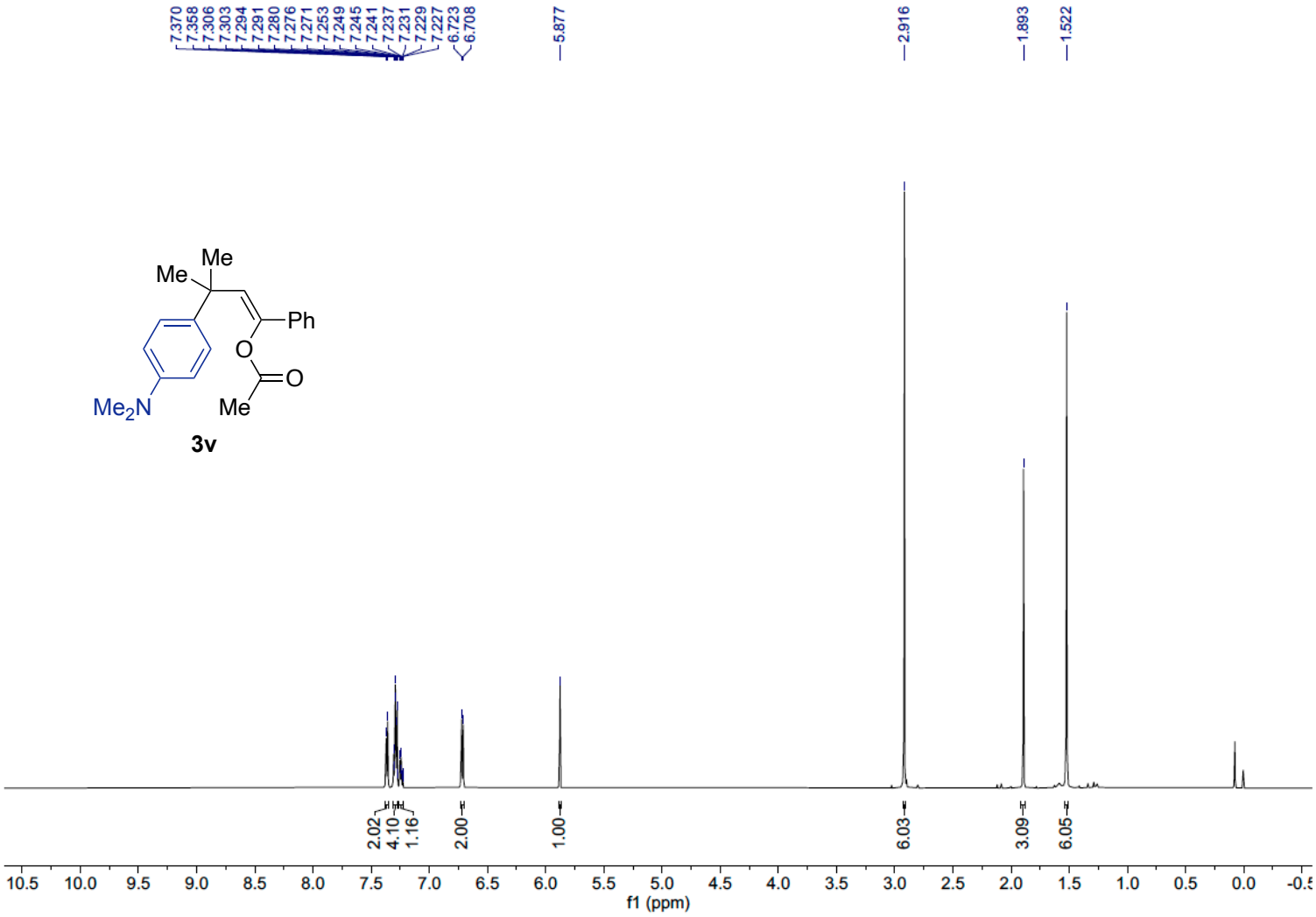
3t

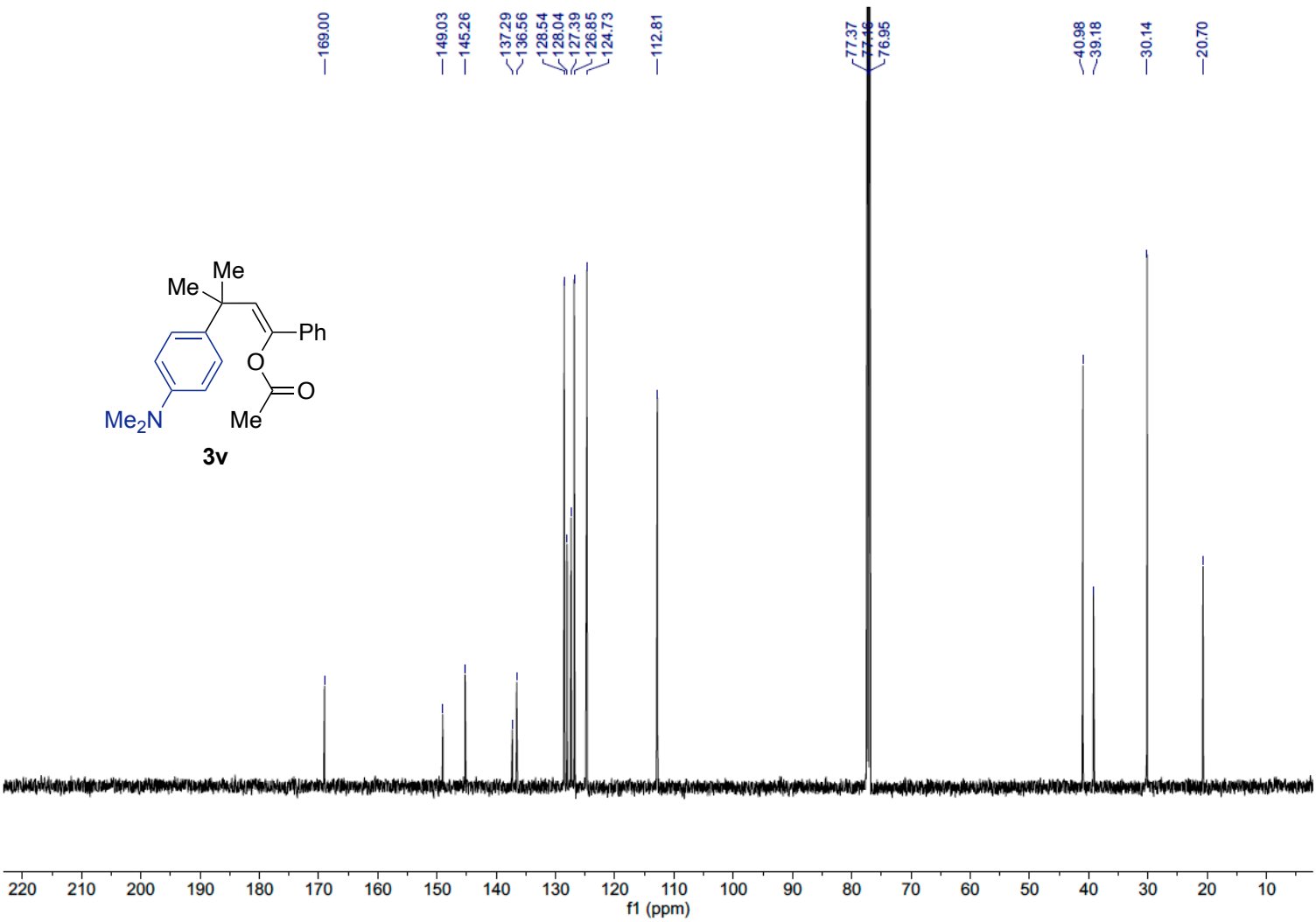

168.75
144.68
136.69
128.53
127.86
127.82
126.20
125.06
124.52
124.05
103.56
77.37
77.16
76.95
35.00
29.91
20.56
12.52
12.01
Me
Me
Me
Ph
Me
N
O
O
Me
Me
f1 (ppm)

3t

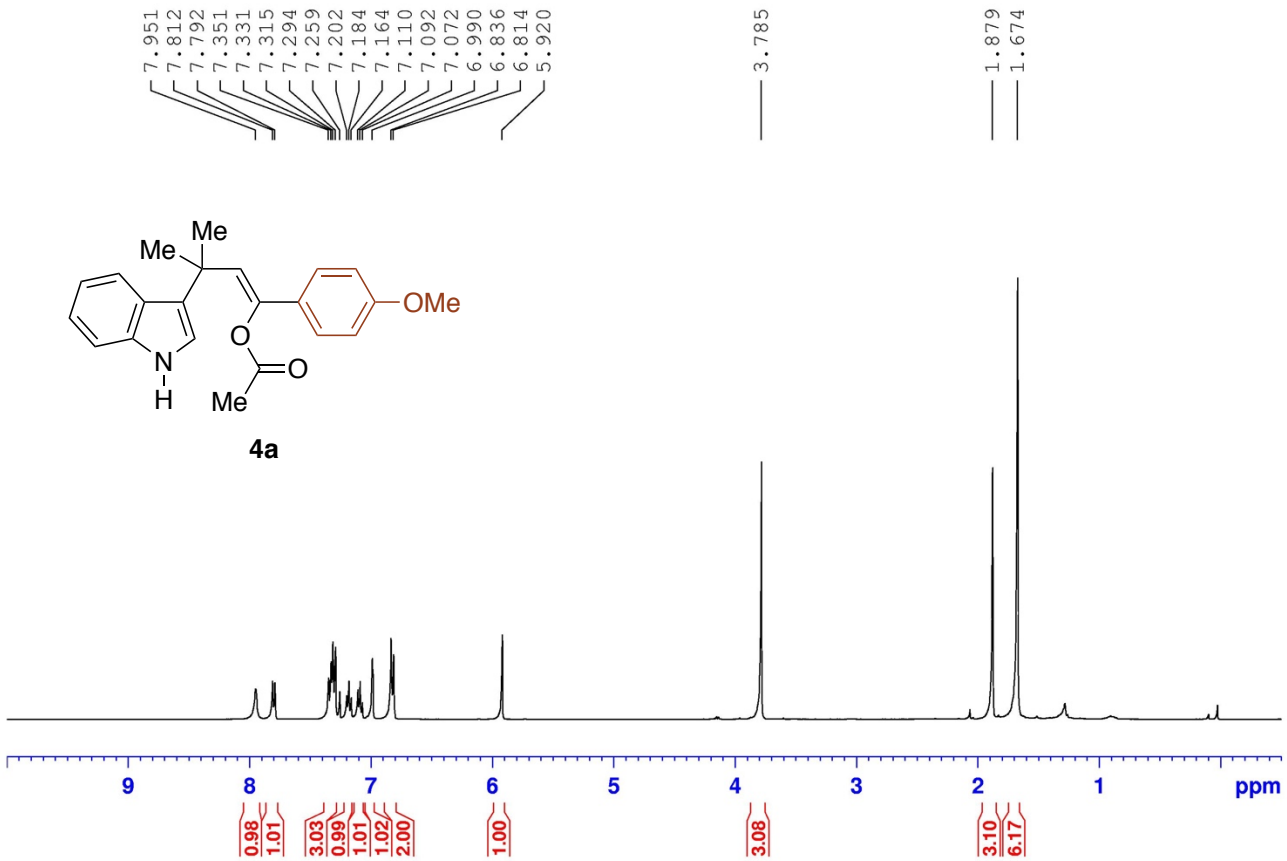

7.349
7.338
7.299
7.287
7.274
7.260
7.232
7.220
7.205
7.193
7.179
6.306
6.290
6.013
3.796
2.929
1.722
1.531
Me
Me
MeO
Ph
O
O
Me
Me2N
3u
2.04
2.04
1.03
1.00
2.06
0.98
3.03
6.09
3.00
6.00
f1 (ppm)


168.68
158.81
150.80
143.69
136.94
128.44
127.53
126.28
125.44
124.42
104.50
98.23
77.38
77.16
76.95
55.53
41.06
37.20
28.96
20.40
Me
Me
MeO
Ph
O
O
Me
Me2N
3u
f1 (ppm)


7.370
7.358
7.306
7.303
7.294
7.291
7.280
7.276
7.271
7.253
7.249
7.245
7.241
7.237
7.231
7.229
7.227
6.723
6.708
5.877
2.916
1.893
1.522
Me
Me
Ph
O
O
Me
Me2N
3v
2.02
4.10
1.16
2.00
1.00
6.03
3.09
6.05
f1 (ppm)

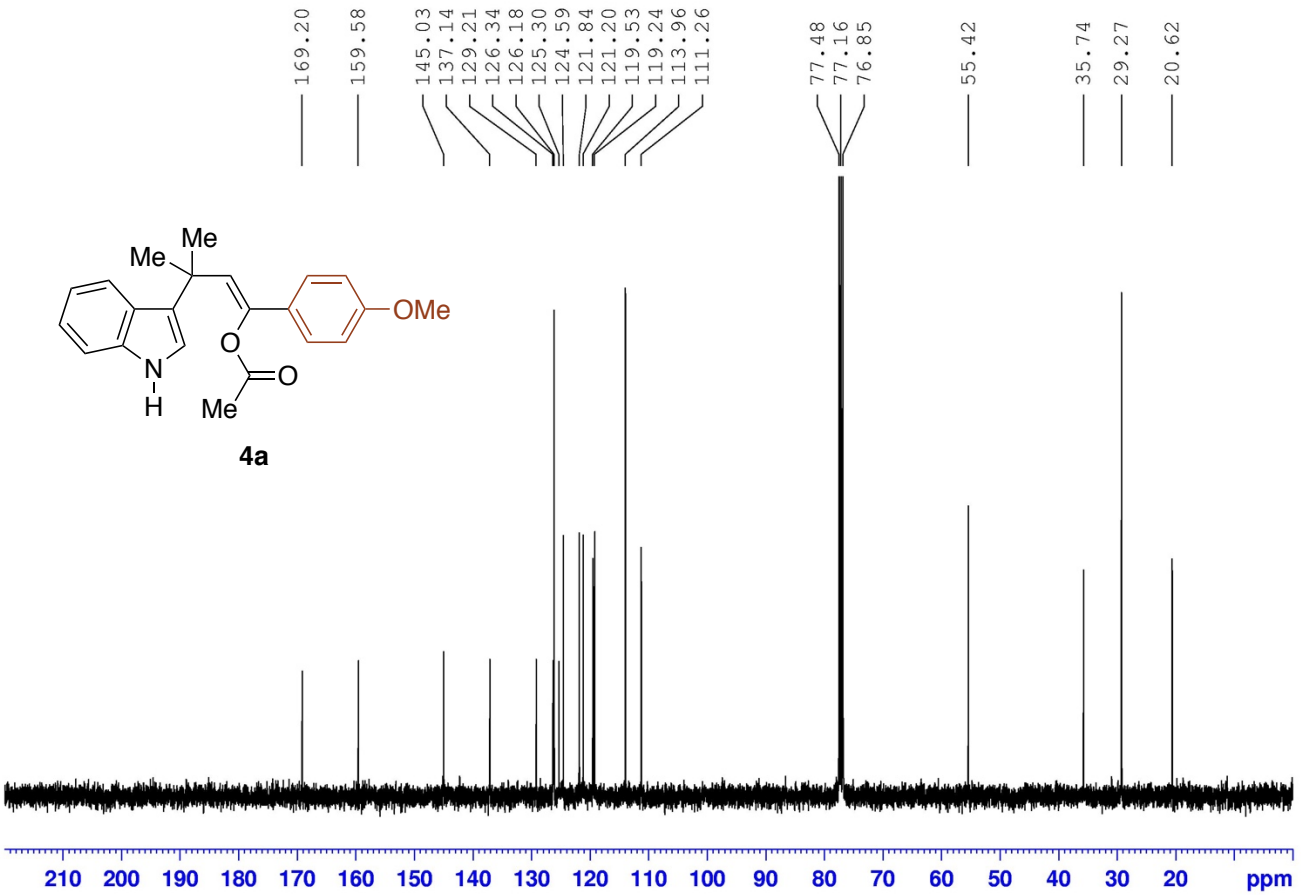

169.00
149.03
145.26
137.29
136.56
128.54
128.04
127.39
126.85
124.73
112.81
77.37
77.16
76.95
40.98
39.18
30.14
20.70
Me
Me
Ph
O
O
Me
Me2N
3v
f1 (ppm)

TSH-Z4 1H AV400

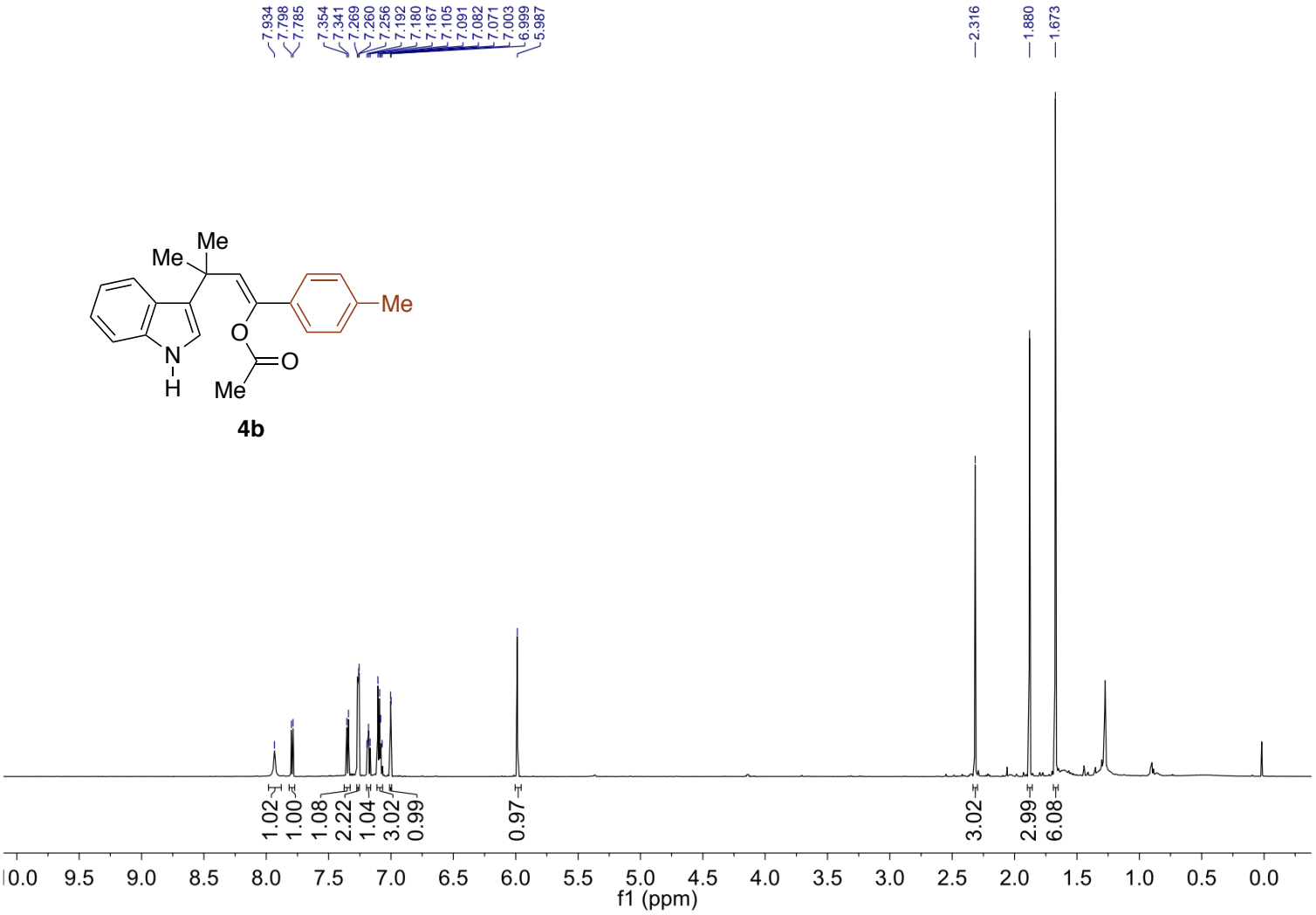


4a

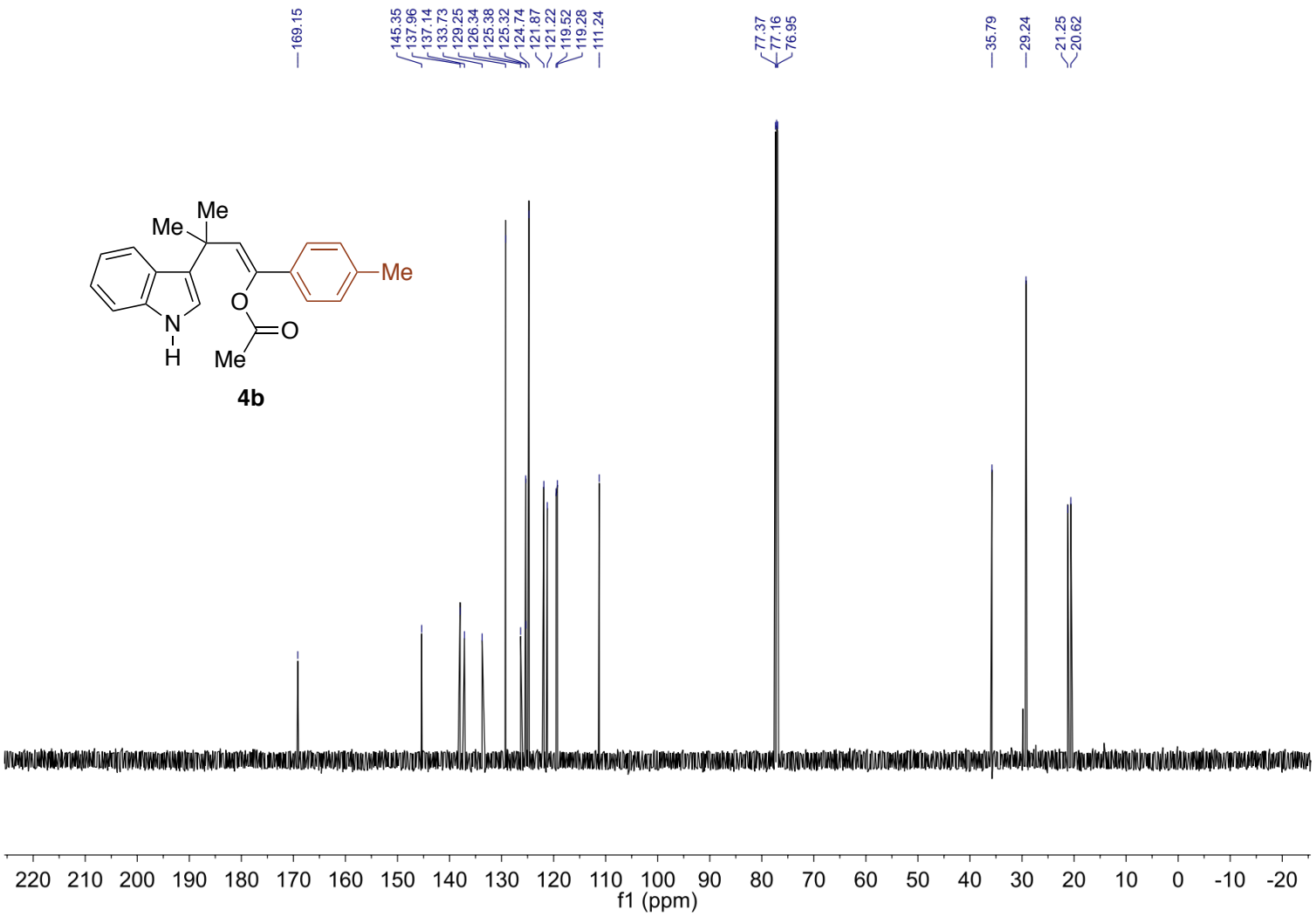
TSH-Z4 13C AV400



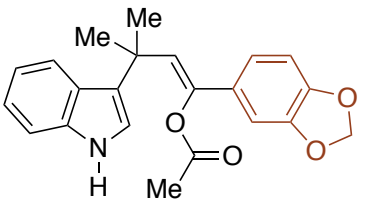
4a


7.934
7.798
7.785
7.354
7.341
7.269
7.260
7.256
7.192
7.180
7.167
7.105
7.091
7.082
7.071
7.003
6.999
5.987
2.316
1.880
1.673
Me
Me
Me
O
O
N
H
Me
1.02
1.00
1.08
2.22
1.04
3.02
0.99
0.97
3.02
2.99
6.08
f1 (ppm)

4b

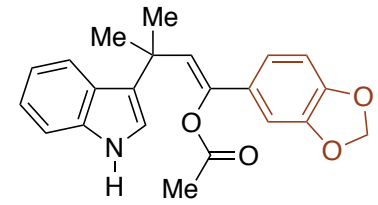

169.15
145.35
137.96
137.14
133.73
129.25
126.34
125.38
125.32
124.74
121.87
121.22
119.52
119.28
111.24
77.37
77.16
76.95
35.79
29.24
21.25
20.62
Me
Me
Me
O
O
N
H
Me
f1 (ppm)

4b


Me
Me
O
O
N
H
O
Me

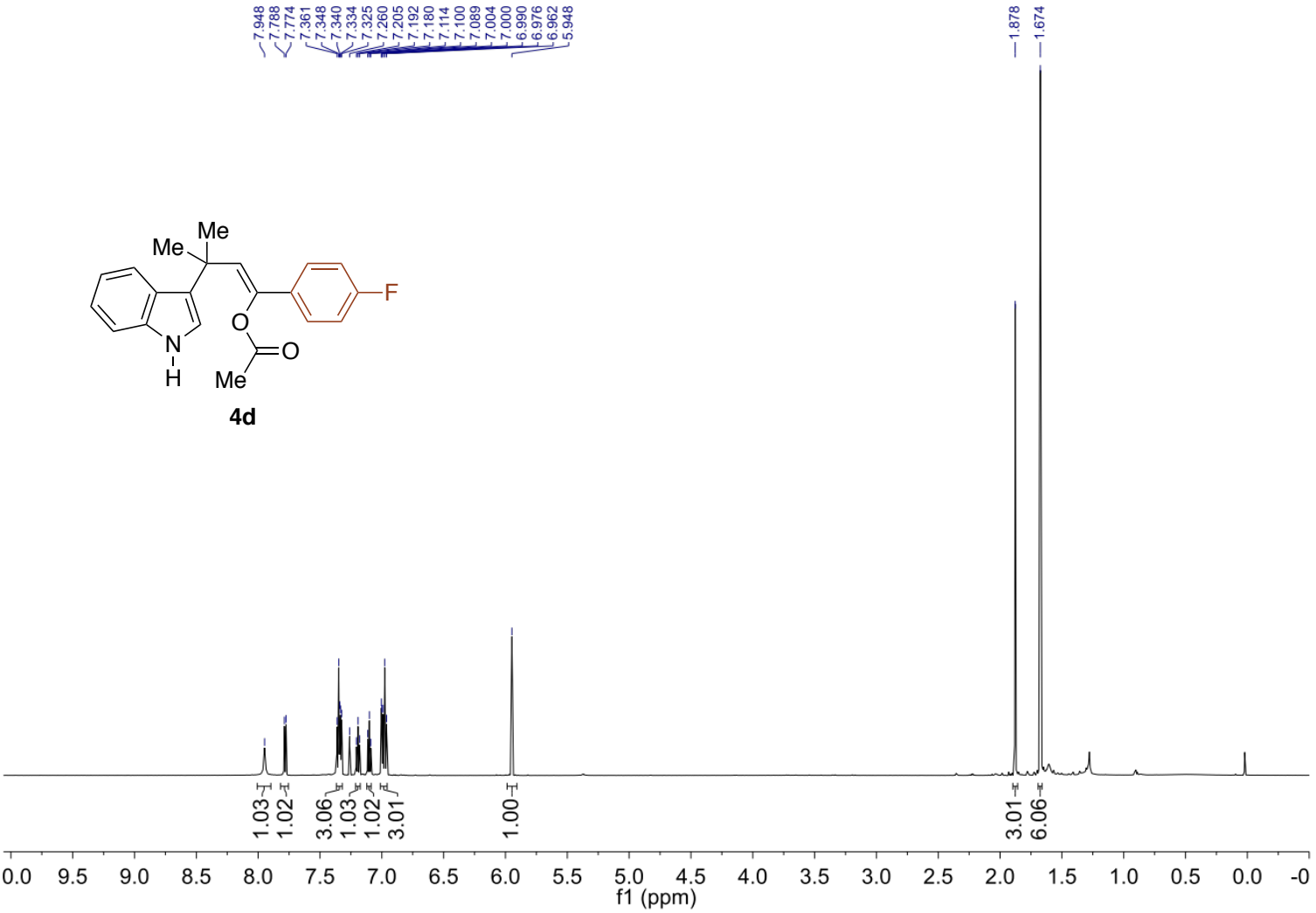
4c

7.954
7.788
7.775
7.350
7.337
7.260
7.196
7.184
7.171
7.107
7.095
7.082
6.991
6.987
6.868
6.865
6.858
6.856
6.731
6.717
5.923
5.887
1.870
1.661
0.98
1.00
1.05
1.03
1.00
1.04
1.99
0.98
2.05
1.00
3.00
6.04
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

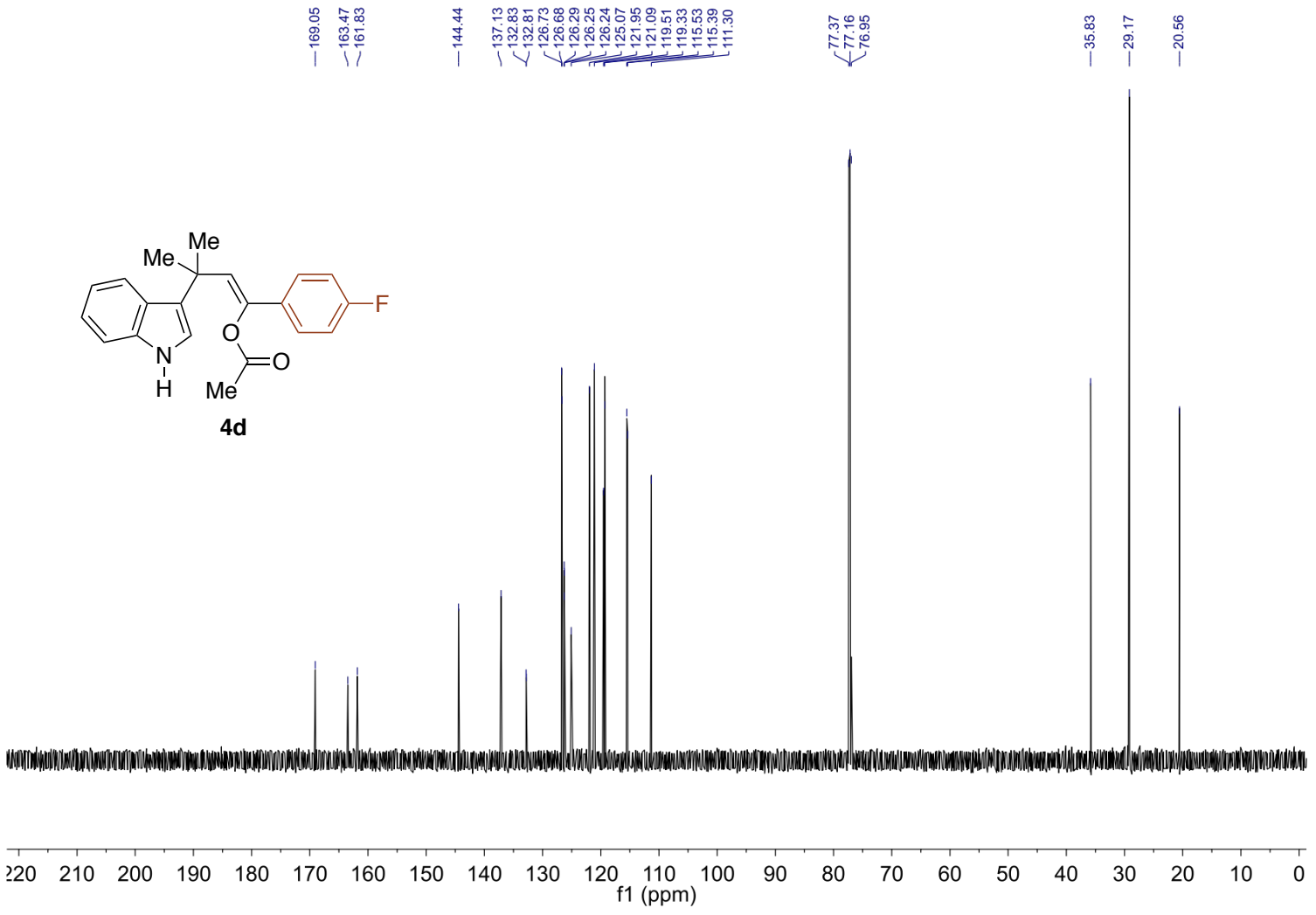

Me
Me
O
O
N
H
O
Me

4c

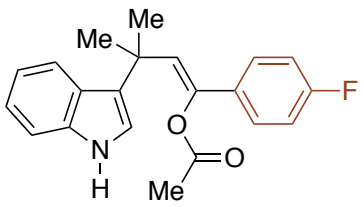
169.13
147.92
147.62
144.94
137.12
131.04
126.30
125.21
121.88
121.13
119.49
119.27
118.75
111.27
108.29
105.65
101.29
77.37
77.16
76.95
35.75
29.21
20.60
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.948
7.788
7.774
7.361
7.348
7.340
7.334
7.325
7.260
7.205
7.192
7.180
7.114
7.100
7.089
7.004
7.000
6.990
6.976
6.962
5.948
1.878
1.674
Me
Me
F
O
N
H
O
Me
1.03
1.02
3.06
1.03
1.02
3.01
1.00
3.01
6.06
f1 (ppm)

4d

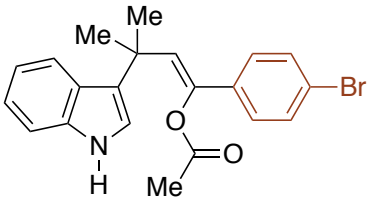

169.05
163.47
161.83
144.44
137.13
132.83
132.81
126.73
126.68
126.29
126.25
126.24
125.07
121.95
121.09
119.51
119.33
115.53
115.39
111.30
77.37
77.16
76.95
35.83
29.17
20.56
Me
Me
F
O
N
H
O
Me
f1 (ppm)

4d


Me
Me
F
O
N
H
O
Me

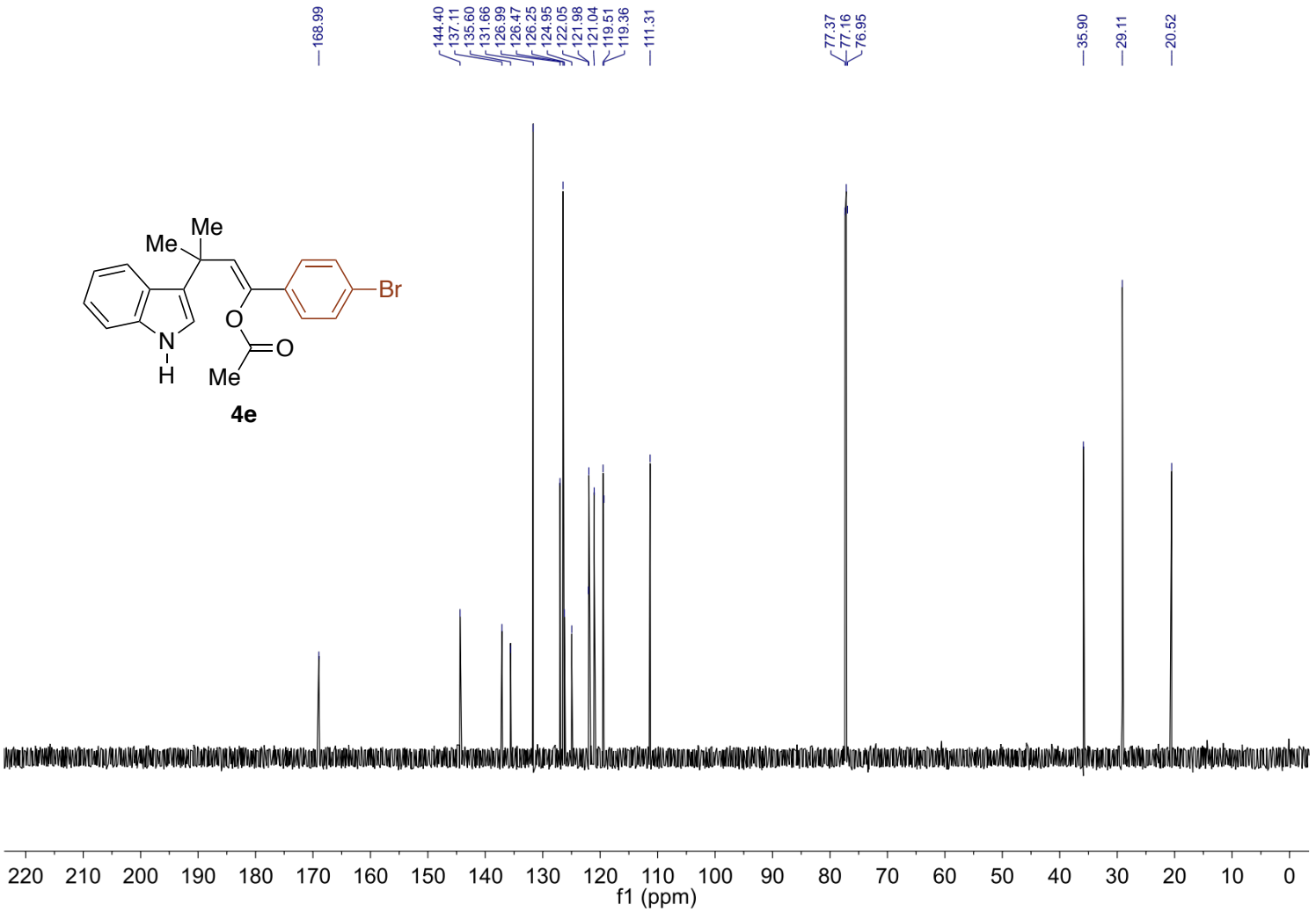
4d

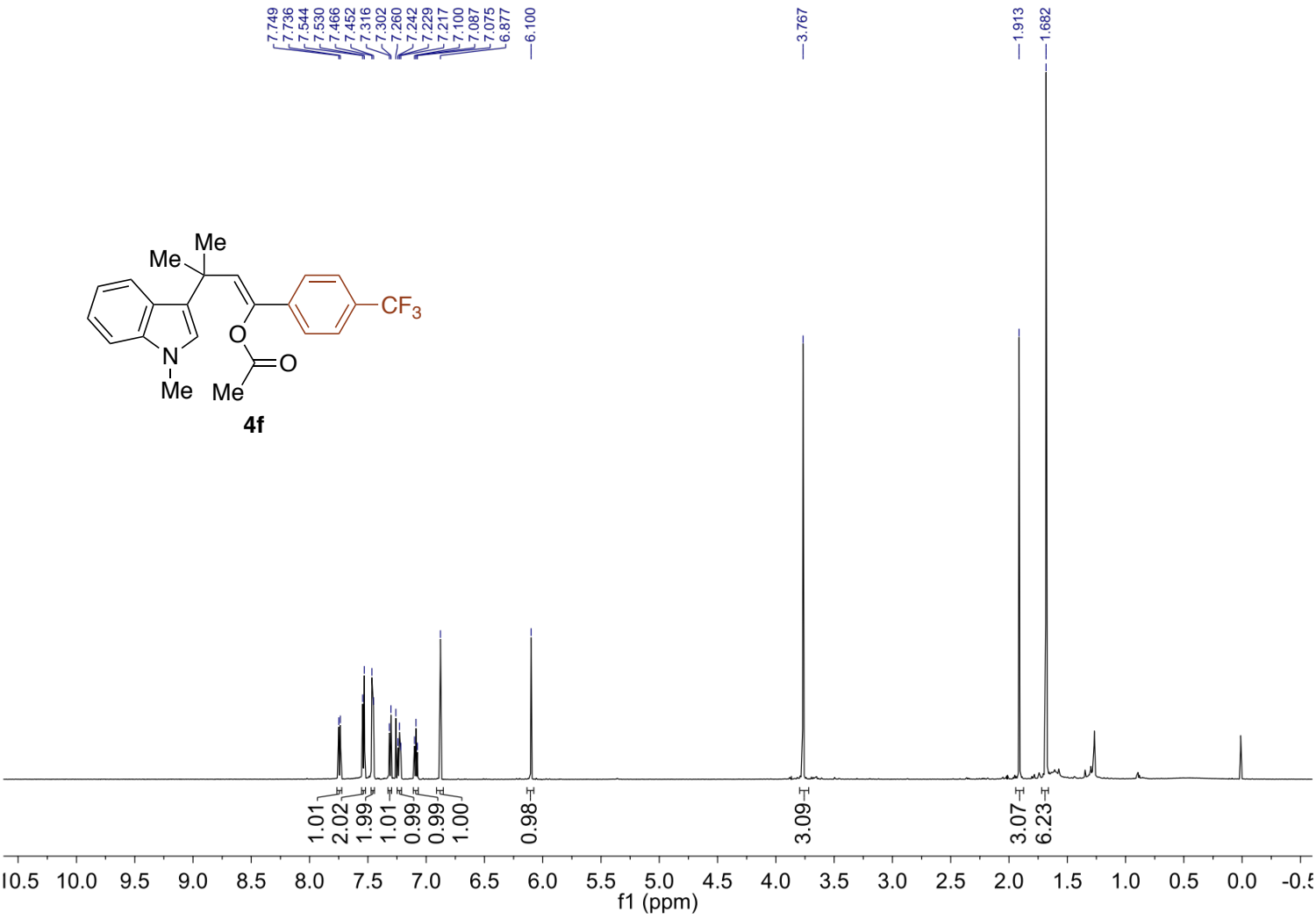
-113.902
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
f1 (ppm)

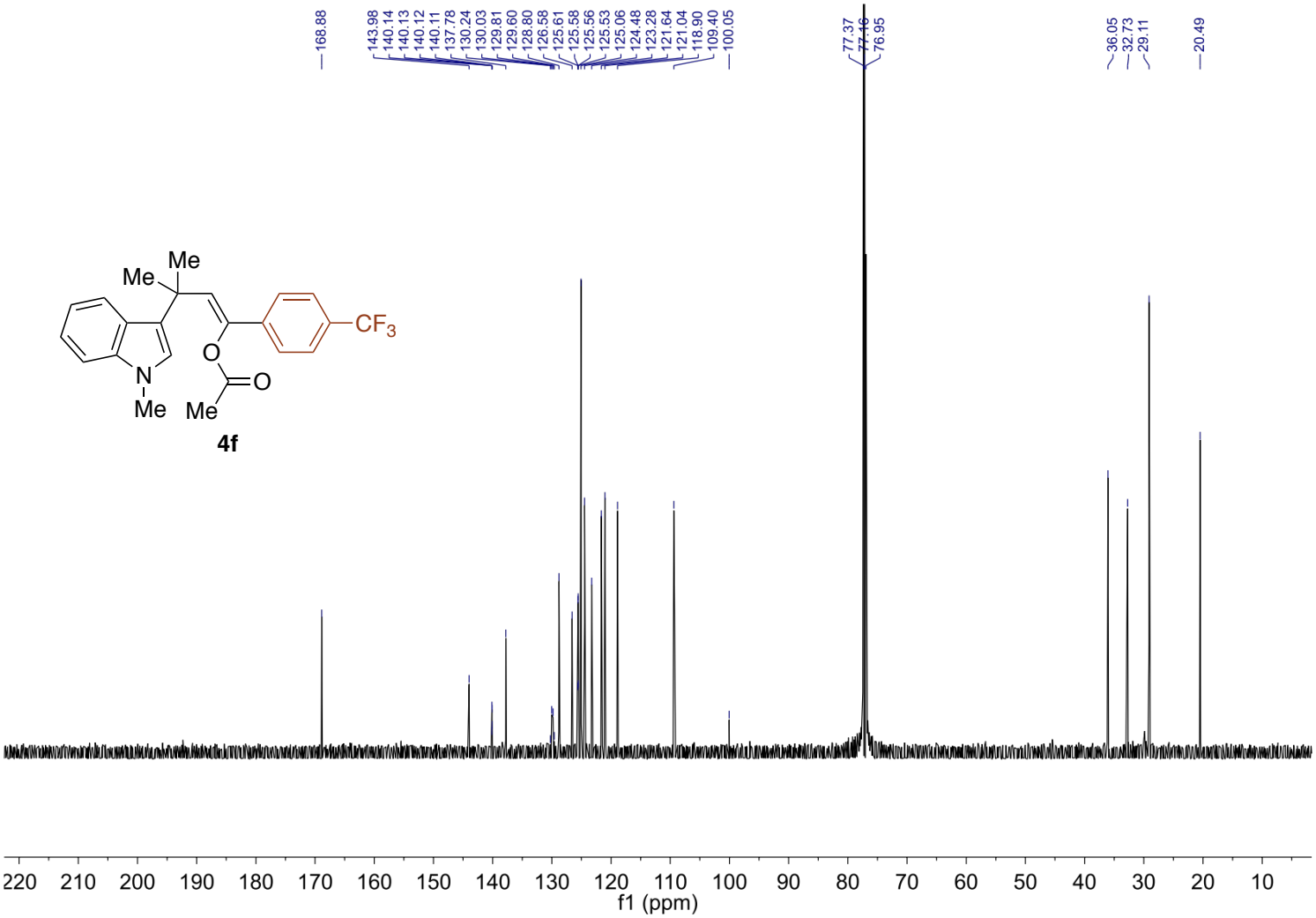

Me
Me
Br
O
N
H
O
Me

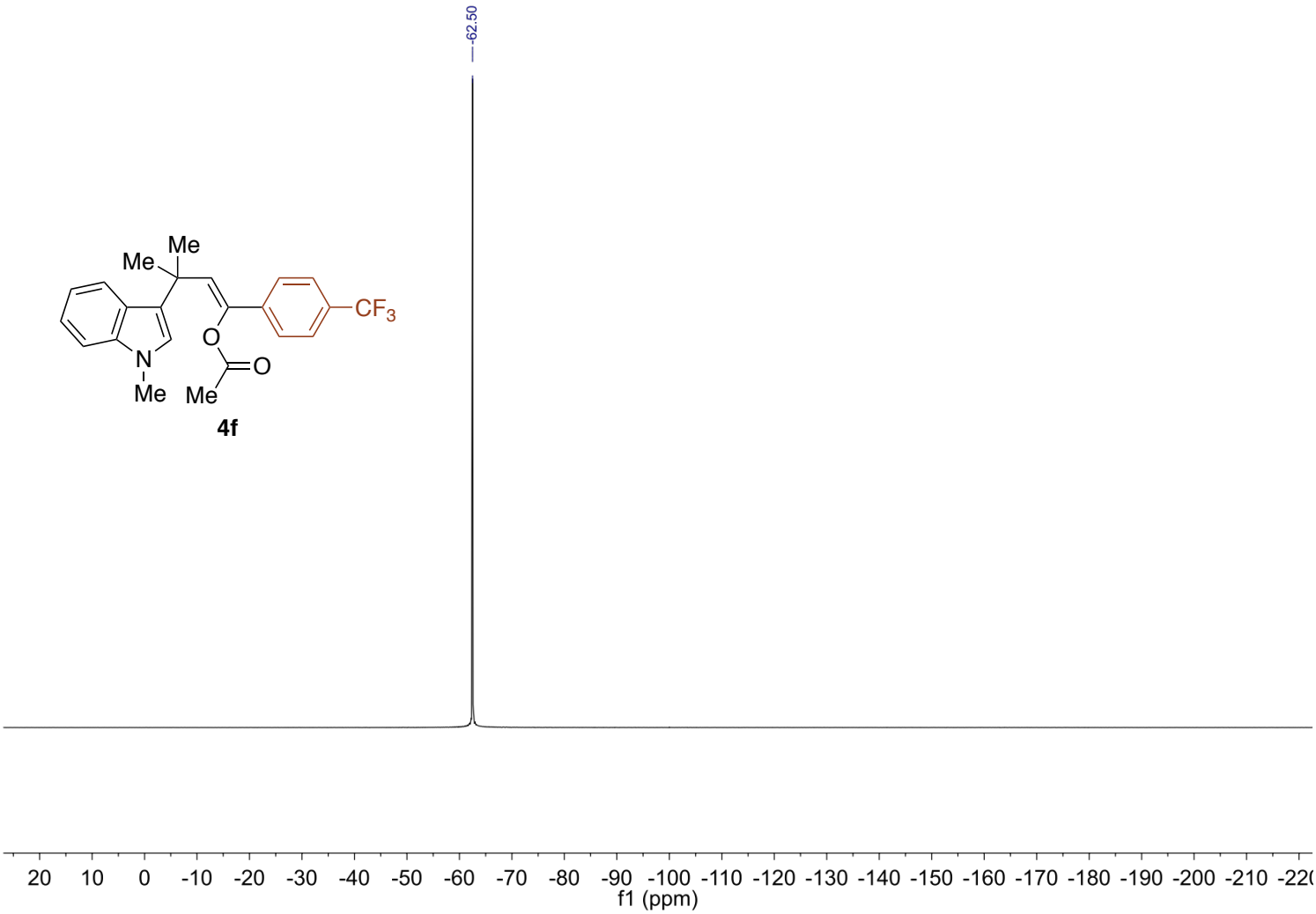
4e

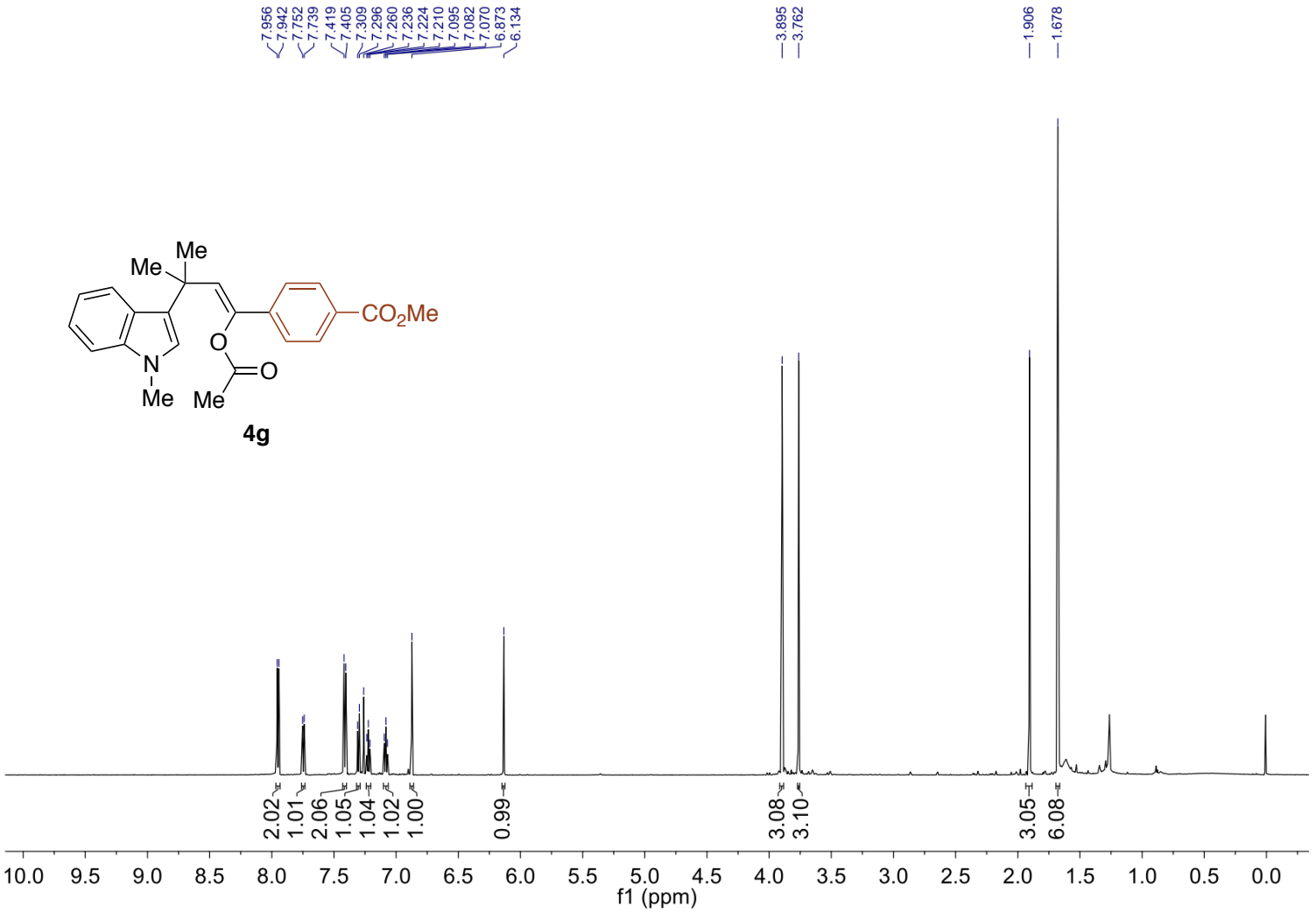
7.949
7.763
7.750
7.415
7.401
7.358
7.345
7.260
7.233
7.219
7.203
7.190
7.177
7.106
7.093
7.081
7.000
6.996
6.012
1.877
1.670
1.00
1.00
1.99
1.04
2.05
1.02
1.05
1.01
1.01
3.01
6.08
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


168.99
144.40
137.11
135.60
131.66
126.99
126.47
126.25
124.95
122.05
121.98
121.04
119.51
119.36
111.31
77.37
77.16
76.95
35.90
29.11
20.52
Me
Me
Br
O
N
H
O
Me
4e
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

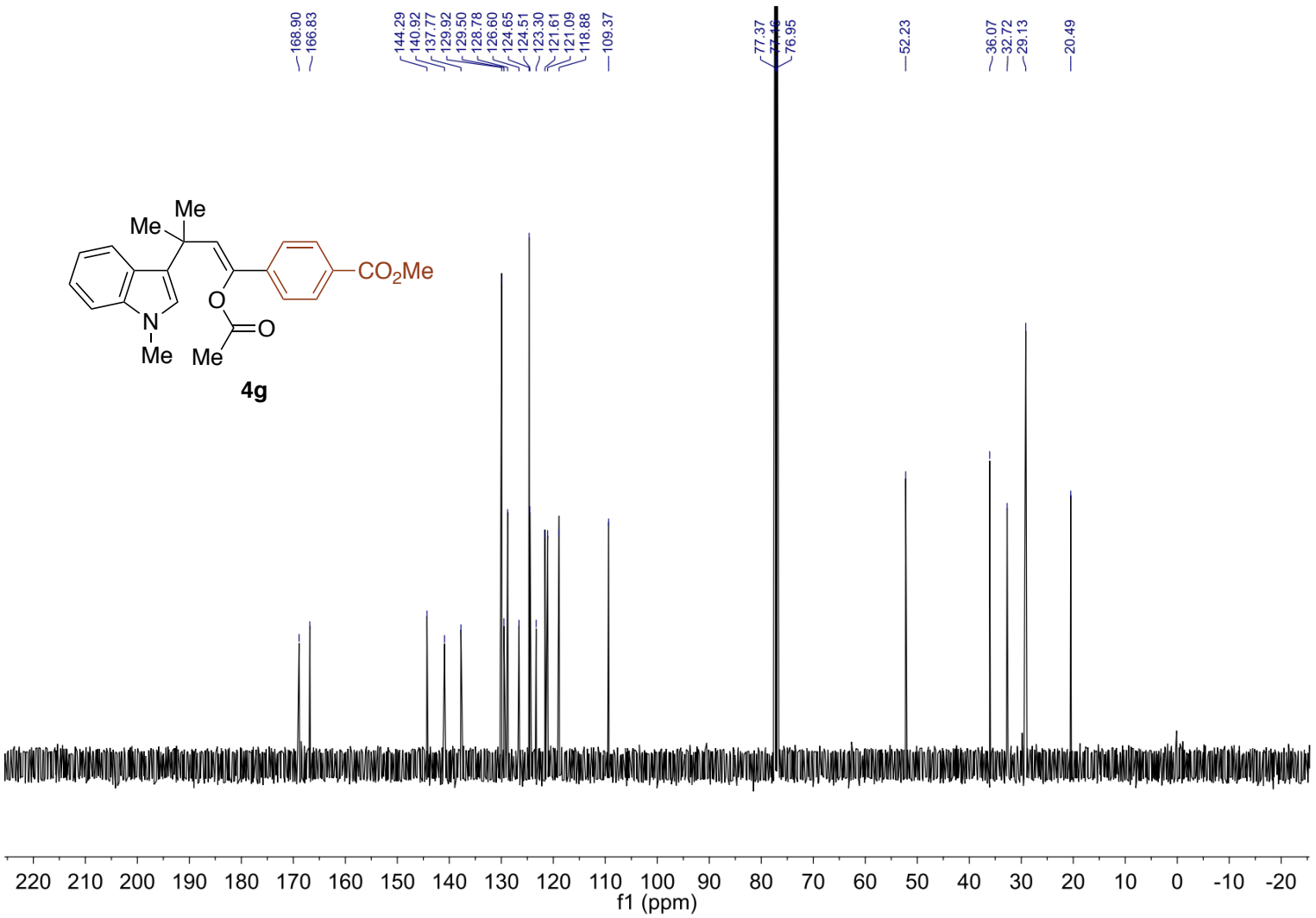

7.749
7.736
7.544
7.530
7.466
7.452
7.316
7.302
7.260
7.242
7.229
7.217
7.100
7.087
7.075
6.877
6.100
3.767
1.913
1.682
Me
Me
CF3
O
N
Me
O
Me
4f
1.01
2.02
1.99
1.01
0.99
0.99
1.00
0.98
3.09
3.07
6.23
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


168.88
143.98
140.14
140.13
140.12
140.11
137.78
130.24
130.03
129.81
129.60
128.80
126.58
125.61
125.58
125.56
125.53
125.06
124.48
123.28
121.64
121.04
118.90
109.40
100.05
77.37
77.16
76.95
36.05
32.73
29.11
20.49
Me
Me
CF3
O
O
N
Me
Me
4f
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

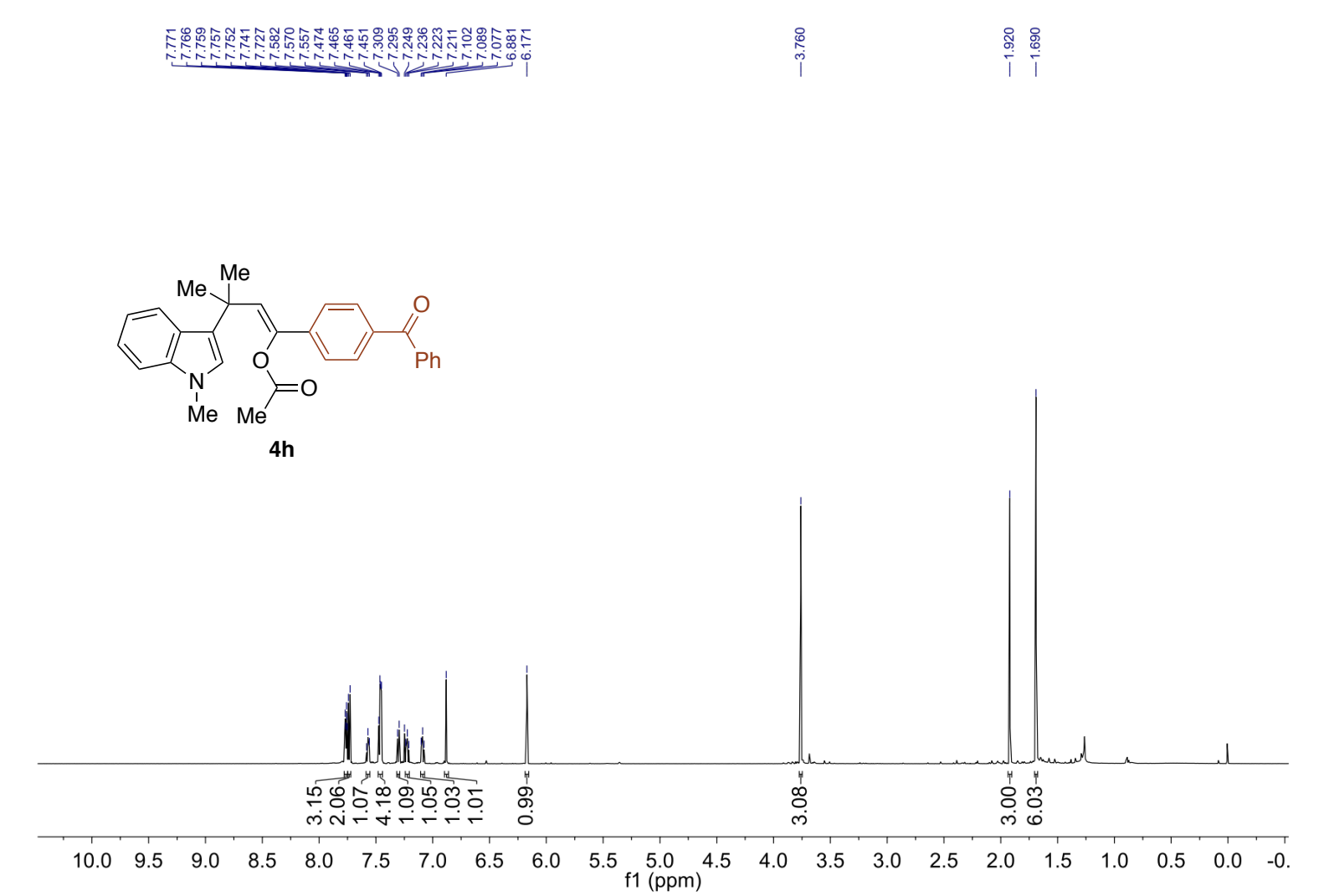

-62.50
Me
Me
CF3
O
O
N
Me
Me
4f
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -22(
f1 (ppm)

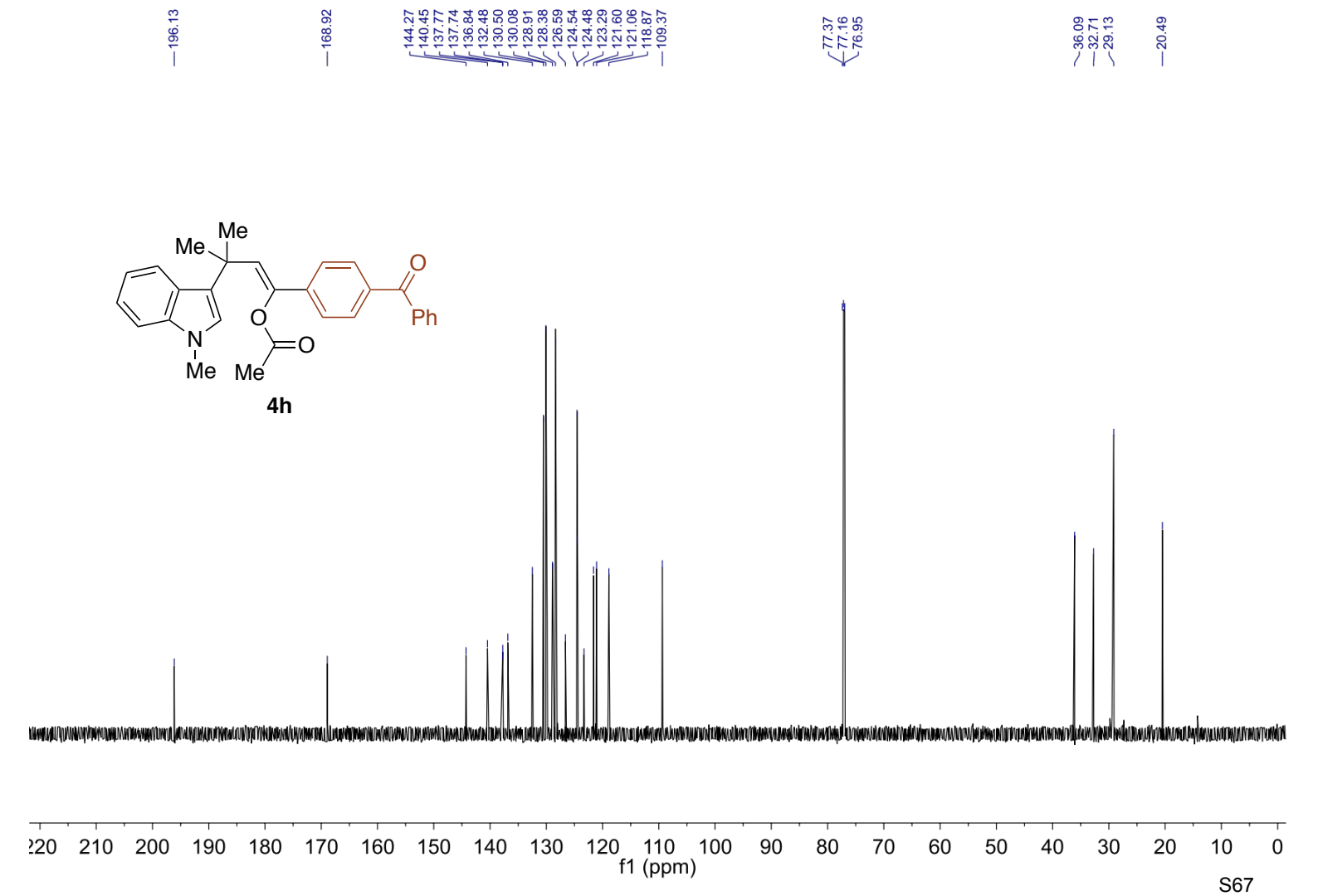

7.956
7.942
7.752
7.739
7.419
7.405
7.309
7.296
7.260
7.236
7.224
7.210
7.095
7.082
7.070
6.873
6.134
3.895
3.762
1.906
1.678
Me
Me
CO2Me
O
O
N
Me
Me
2.02
1.01
2.06
1.05
1.04
1.02
1.00
0.99
3.08
3.10
3.05
6.08
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

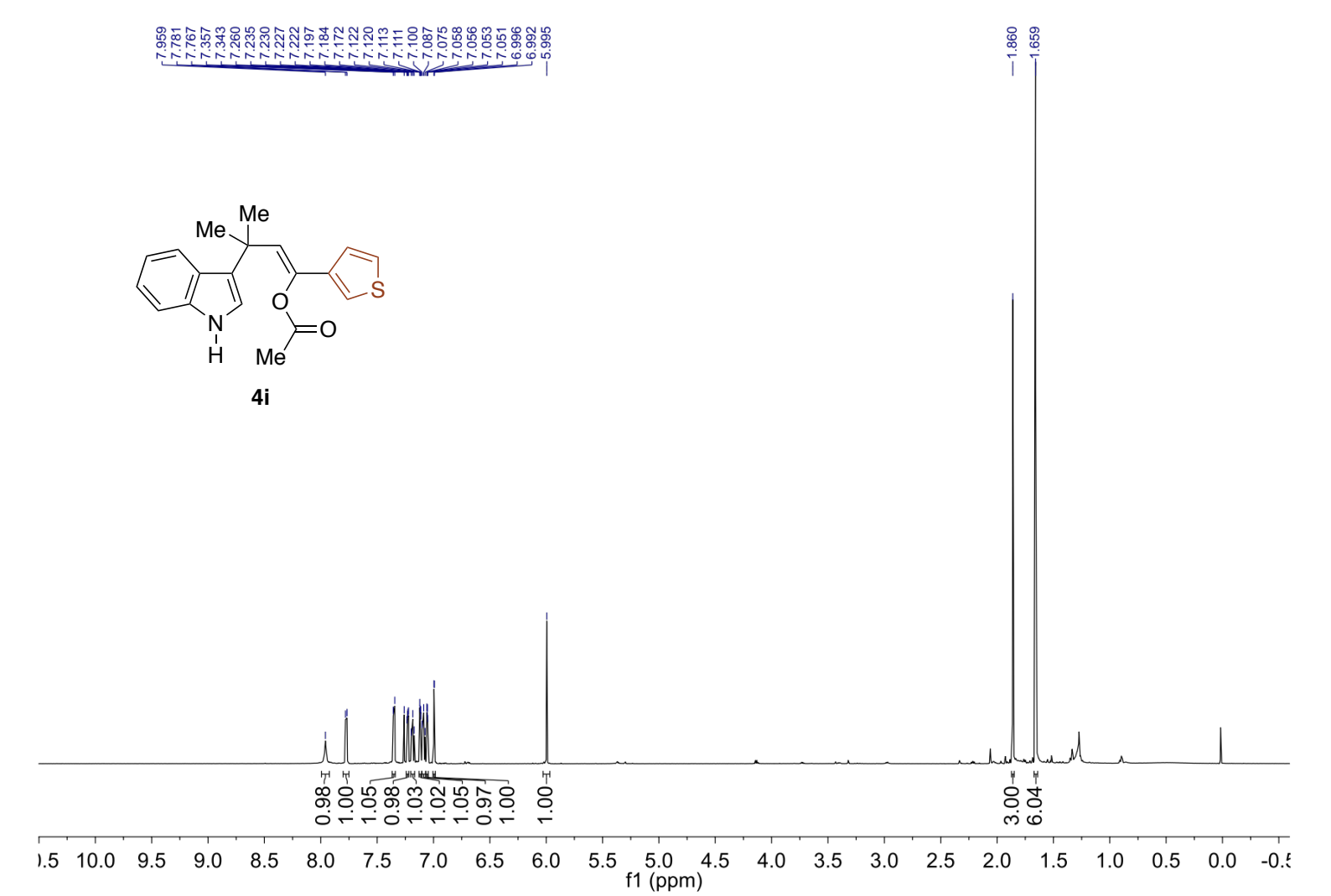
4g


168.90
166.83
144.29
140.92
137.77
129.92
129.50
128.78
126.60
124.65
124.51
123.30
121.61
121.09
118.88
109.37
77.37
77.16
76.95
52.23
36.07
32.72
29.13
20.49
Me
Me
CO2Me
O
O
N
Me
Me
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

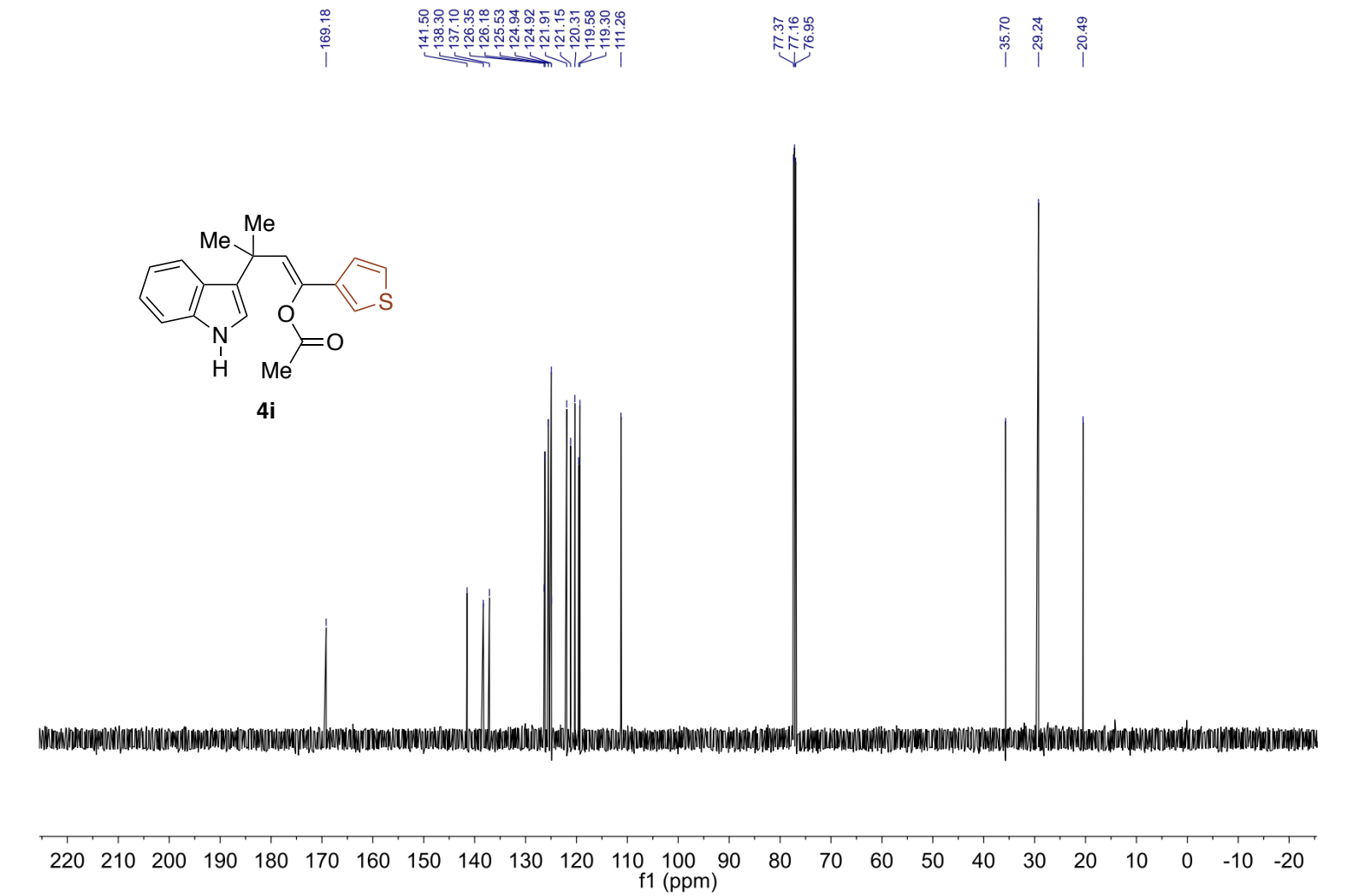
4g


7.771
7.766
7.759
7.757
7.752
7.741
7.727
7.582
7.570
7.557
7.474
7.465
7.461
7.451
7.309
7.295
7.249
7.236
7.223
7.211
7.102
7.089
7.077
6.881
6.171
3.760
1.920
1.690
Me
Me
O
Ph
O
N
Me
O
Me
4h
3.15
2.06
1.07
4.18
1.09
1.05
1.03
1.01
0.99
3.08
3.00
6.03
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)

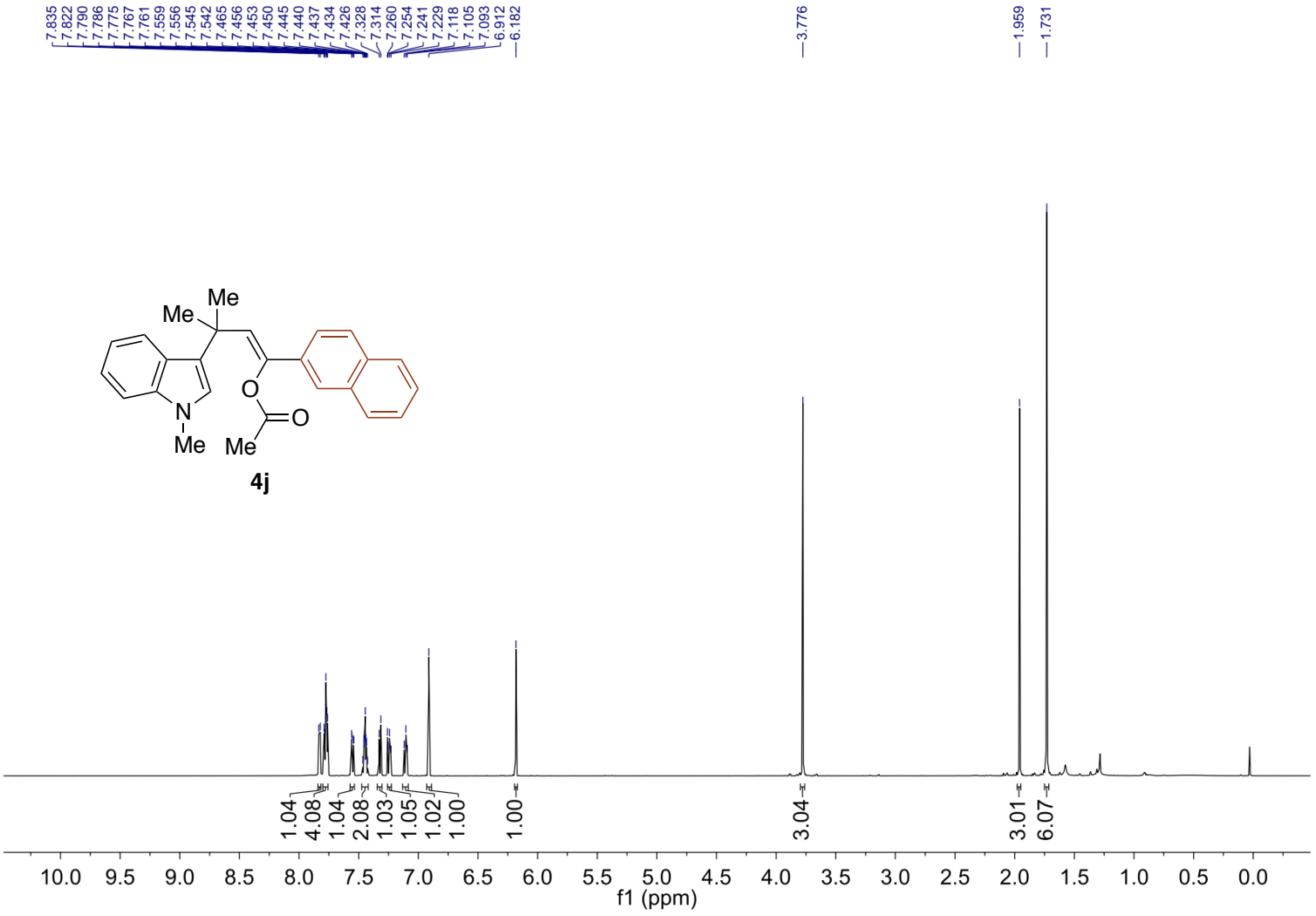

196.13
168.92
144.27
140.45
137.77
137.74
136.84
132.48
130.50
130.08
128.91
128.38
126.59
124.54
124.48
123.29
121.60
121.06
118.87
109.37
77.37
77.16
76.95
36.09
32.71
29.13
20.49
Me
Me
O
Ph
O
N
Me
O
Me
4h
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

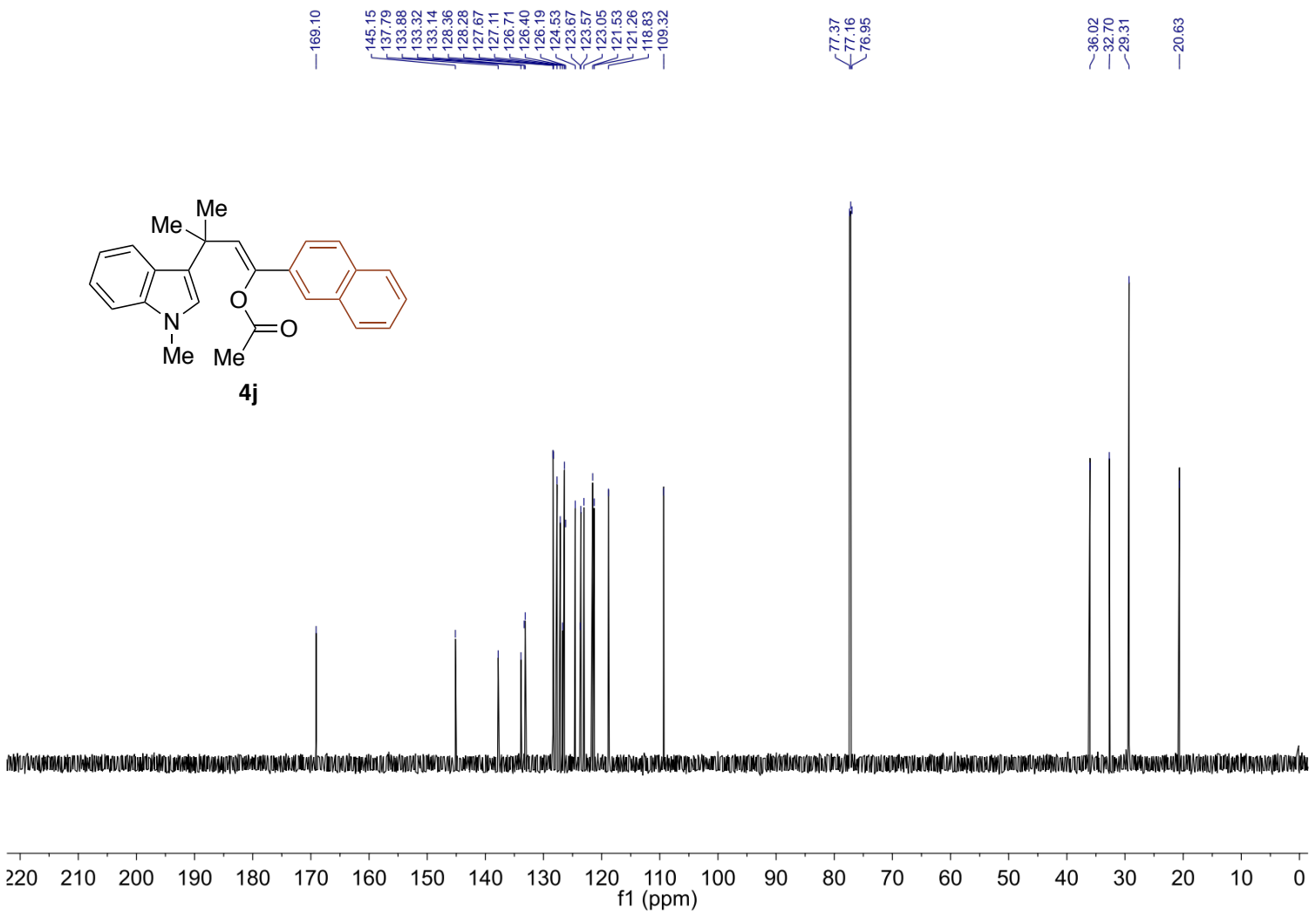

7.959
7.781
7.767
7.357
7.343
7.260
7.235
7.230
7.227
7.222
7.197
7.184
7.172
7.122
7.120
7.113
7.111
7.100
7.087
7.075
7.058
7.056
7.053
7.051
6.996
6.992
5.995
1.860
1.659
Me
Me
S
O
N
H
O
Me
0.98
1.00
1.05
0.98
1.03
1.02
1.05
0.97
1.00
1.00
3.00
6.04
f1 (ppm)

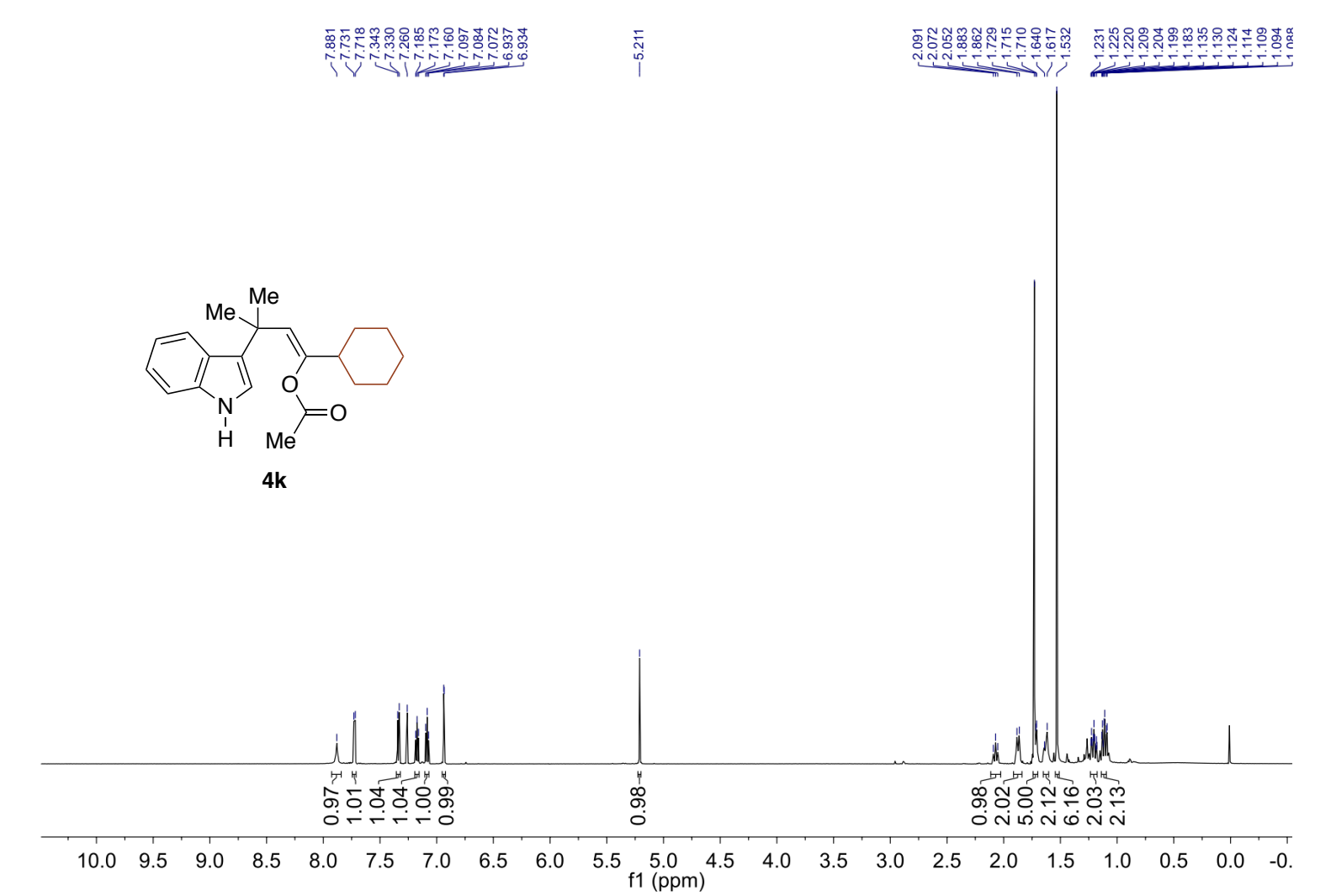
4i


169.18
141.50
138.30
137.10
126.35
126.18
125.53
124.94
124.92
121.91
121.15
120.31
119.58
119.30
111.26
77.37
77.16
76.95
35.70
29.24
20.49
Me
Me
S
O
N
H
O
Me
f1 (ppm)

4i

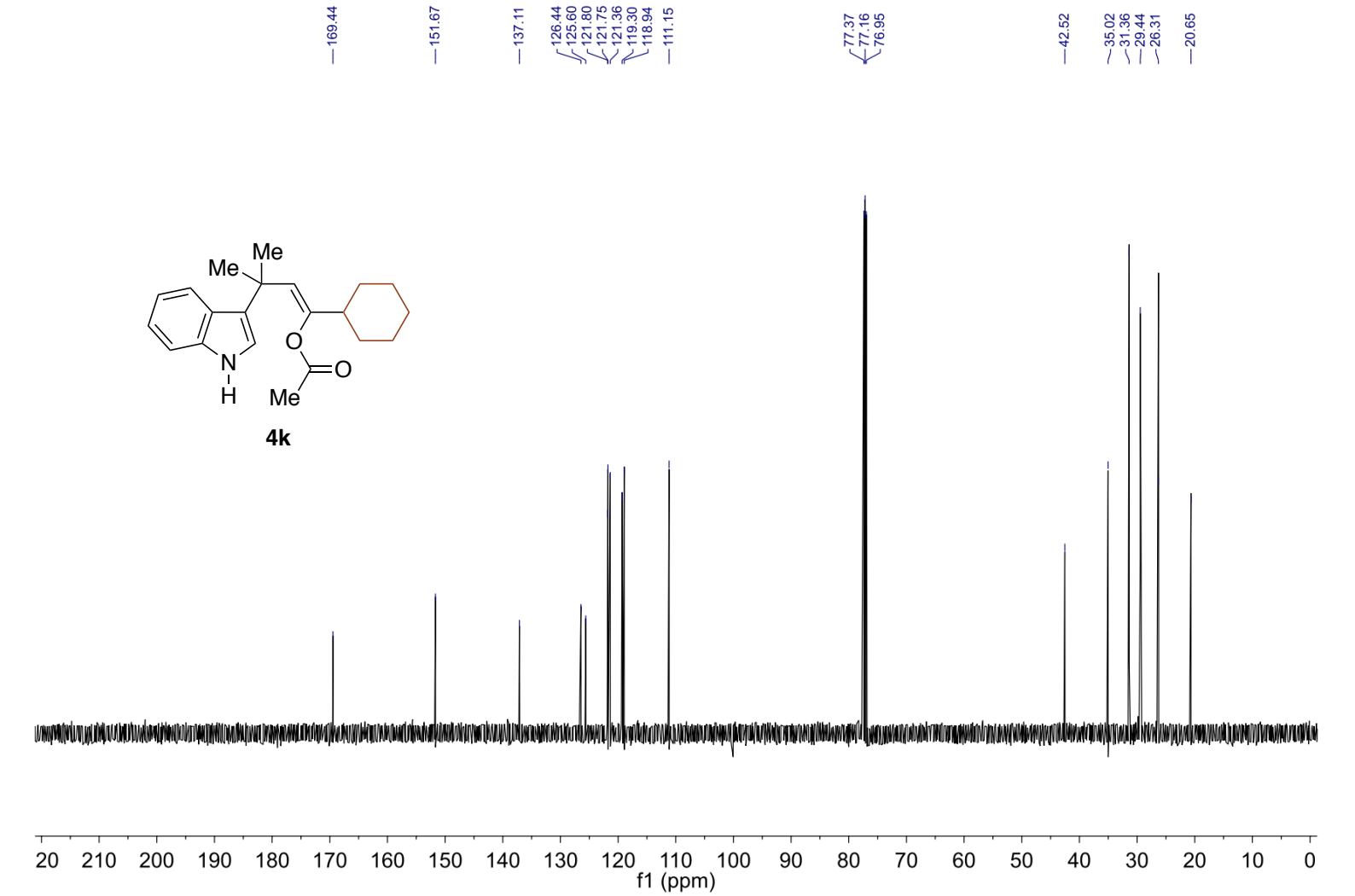

7.835
7.822
7.790
7.786
7.775
7.767
7.761
7.559
7.556
7.545
7.542
7.465
7.456
7.453
7.450
7.445
7.440
7.437
7.434
7.426
7.328
7.314
7.260
7.254
7.241
7.229
7.118
7.105
7.093
6.912
6.182
3.776
1.959
1.731
Me
Me
O
N
Me
O
Me
4j
1.04
4.08
1.04
2.08
1.03
1.05
1.02
1.00
1.00
3.04
3.01
6.07
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


169.10
145.15
137.79
133.88
133.32
133.14
128.36
128.28
127.67
127.11
126.71
126.40
126.19
124.53
123.67
123.57
123.05
121.53
121.26
118.83
109.32
77.37
77.16
76.95
36.02
32.70
29.31
20.63
Me
Me
O
N
Me
O
Me
4j
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.881
7.731
7.718
7.343
7.330
7.260
7.185
7.173
7.160
7.097
7.084
7.072
6.937
6.934
5.211
2.091
2.072
2.052
1.883
1.862
1.729
1.715
1.710
1.640
1.617
1.532
1.231
1.225
1.220
1.209
1.204
1.199
1.183
1.135
1.130
1.124
1.114
1.109
1.094
0.97
1.01
1.04
1.04
1.00
0.99
0.98
0.98
2.02
5.00
2.12
6.16
2.03
2.13
f1 (ppm)

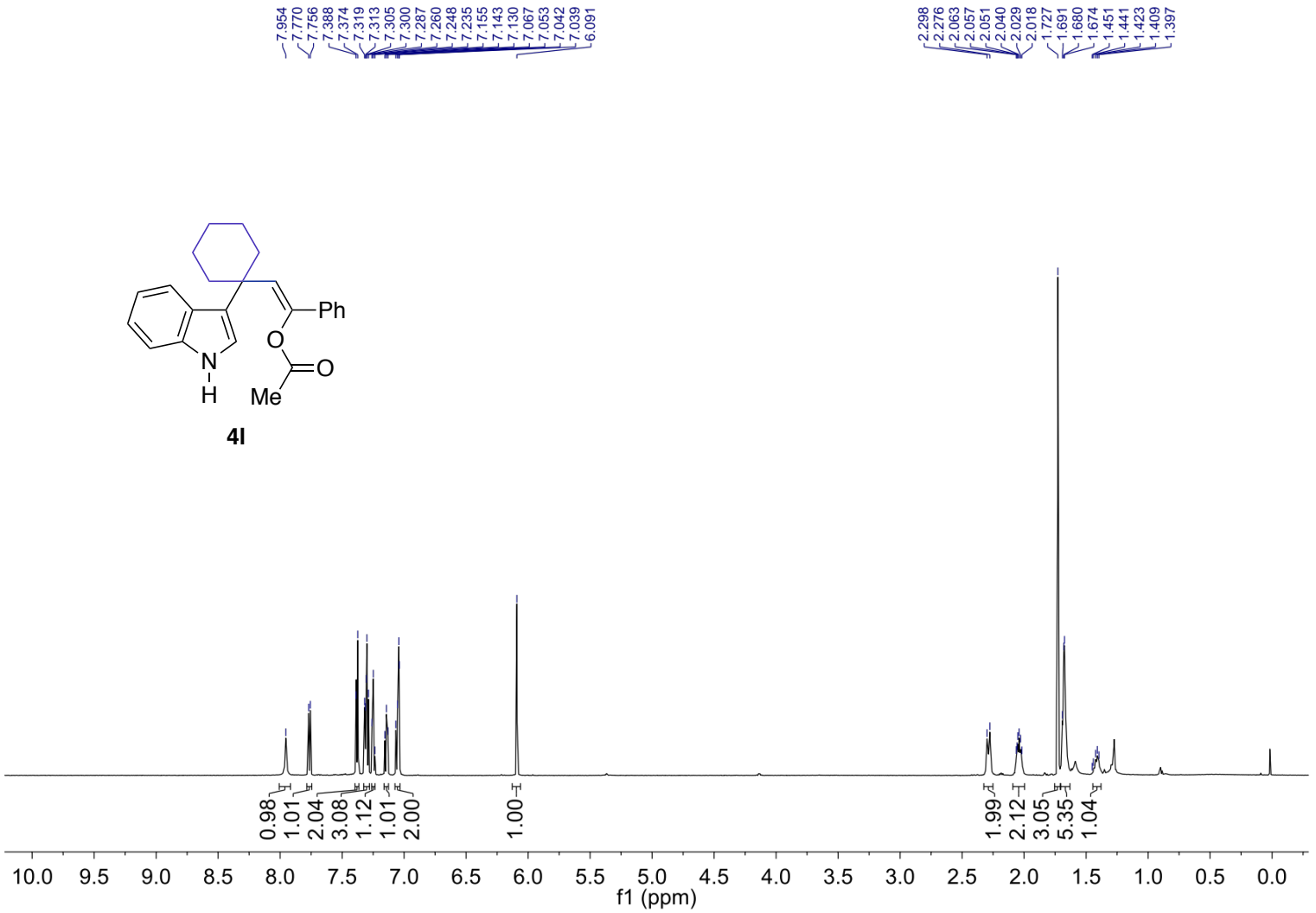
Me
Me
O
O
N
H
Me

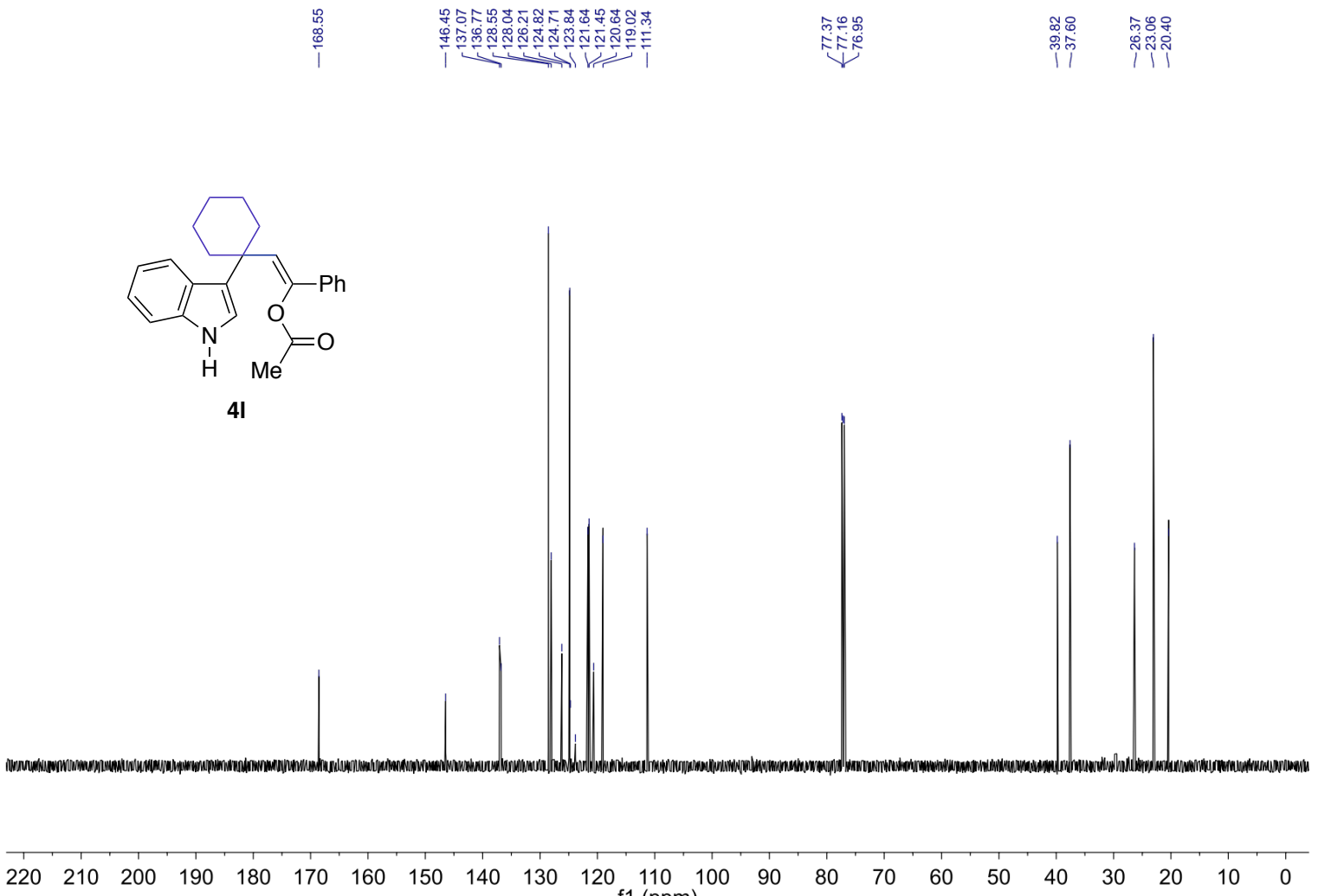
4k

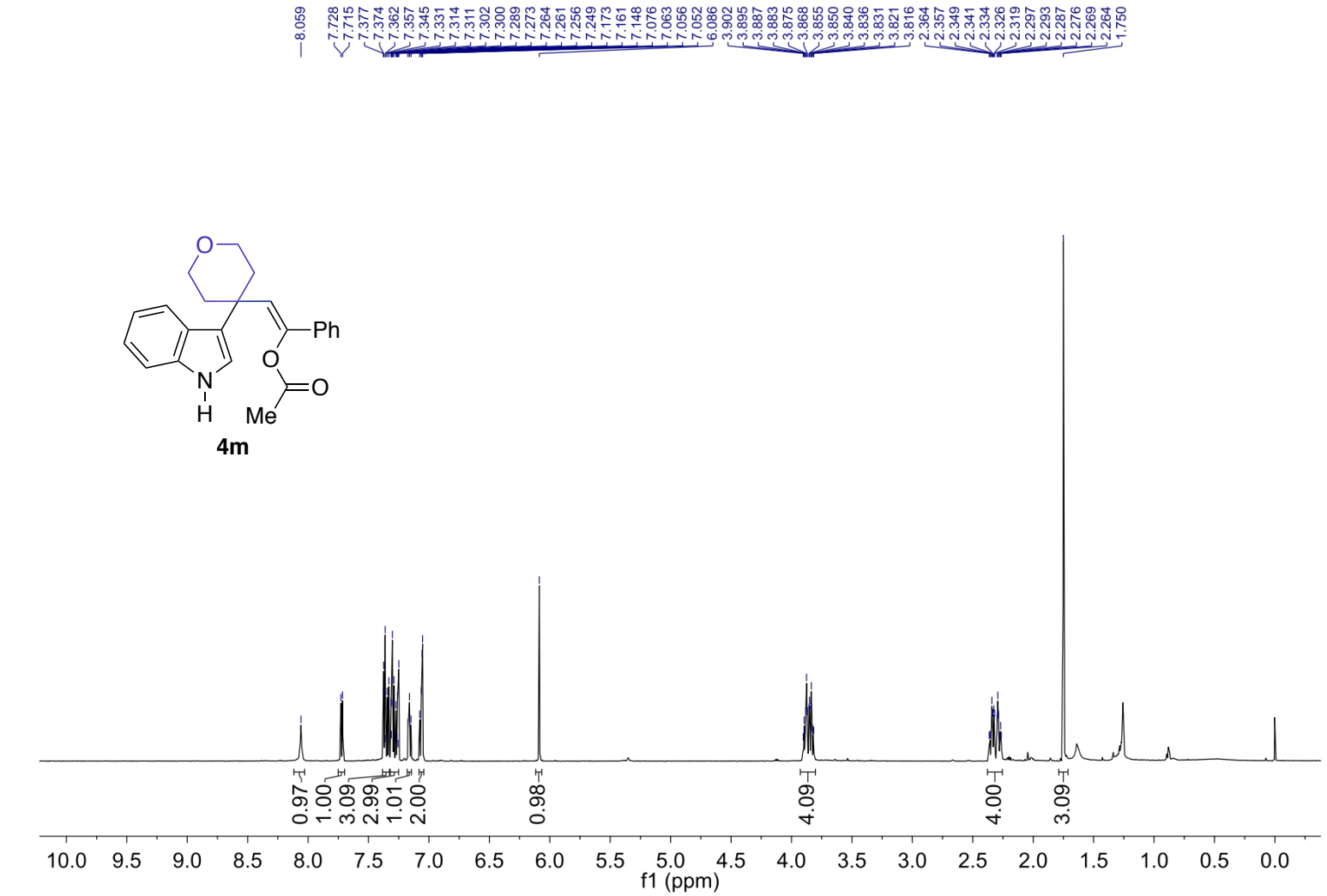

169.44
151.67
137.11
126.44
125.60
121.80
121.75
121.36
119.30
118.94
111.15
77.37
77.16
76.95
42.52
35.02
31.36
29.44
26.31
20.65
f1 (ppm)

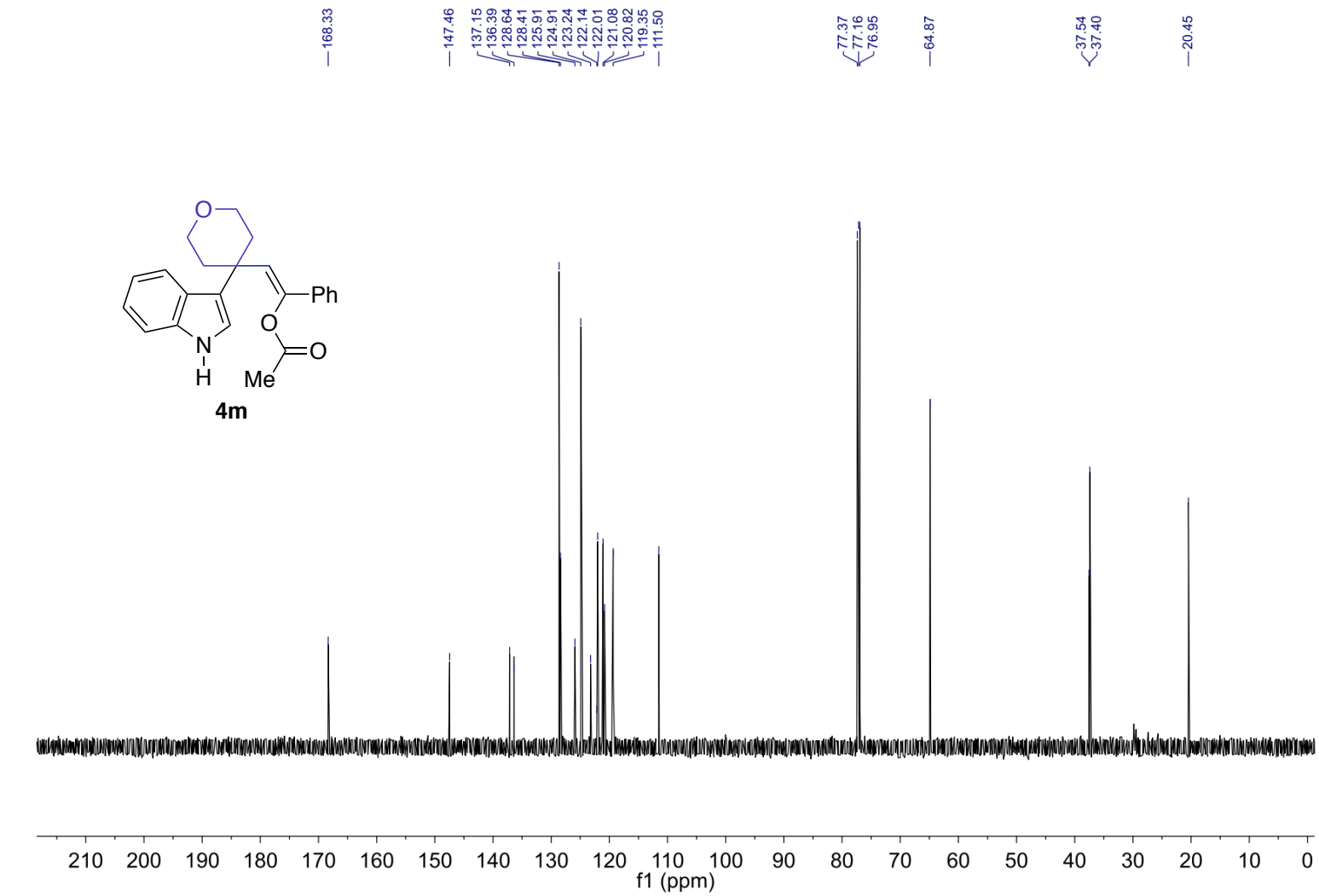
Me
Me
O
O
N
H
Me

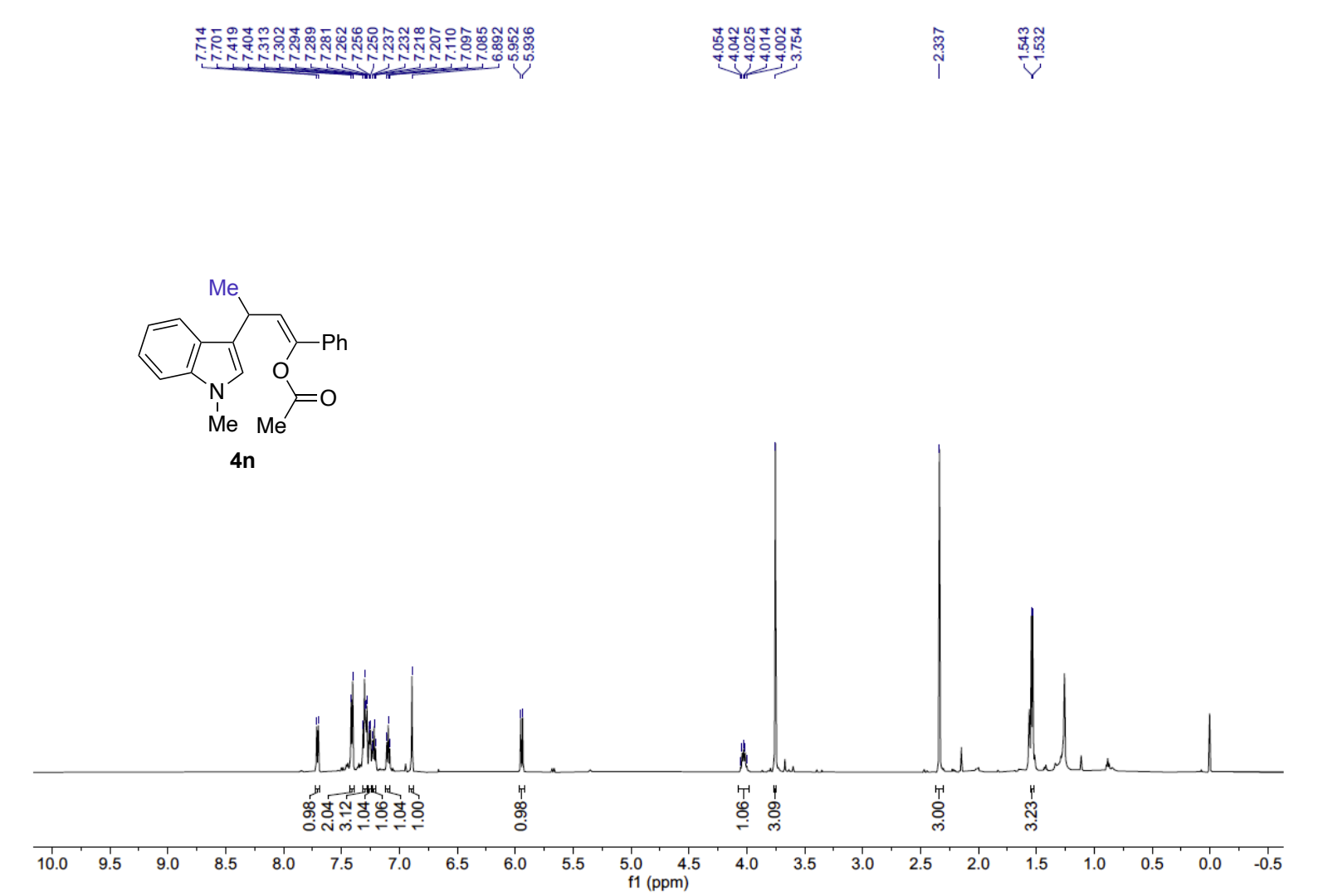
4k


7.954
7.770
7.756
7.388
7.374
7.319
7.313
7.305
7.300
7.287
7.260
7.248
7.235
7.155
7.143
7.130
7.067
7.053
7.042
7.039
6.091
2.298
2.276
2.063
2.057
2.051
2.040
2.029
2.018
1.727
1.691
1.680
1.674
1.451
1.441
1.423
1.409
1.397
Ph
O
N
H
Me
O
4l
0.98
1.01
2.04
3.08
1.12
1.01
2.00
1.00
1.99
2.12
3.05
5.35
1.04
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

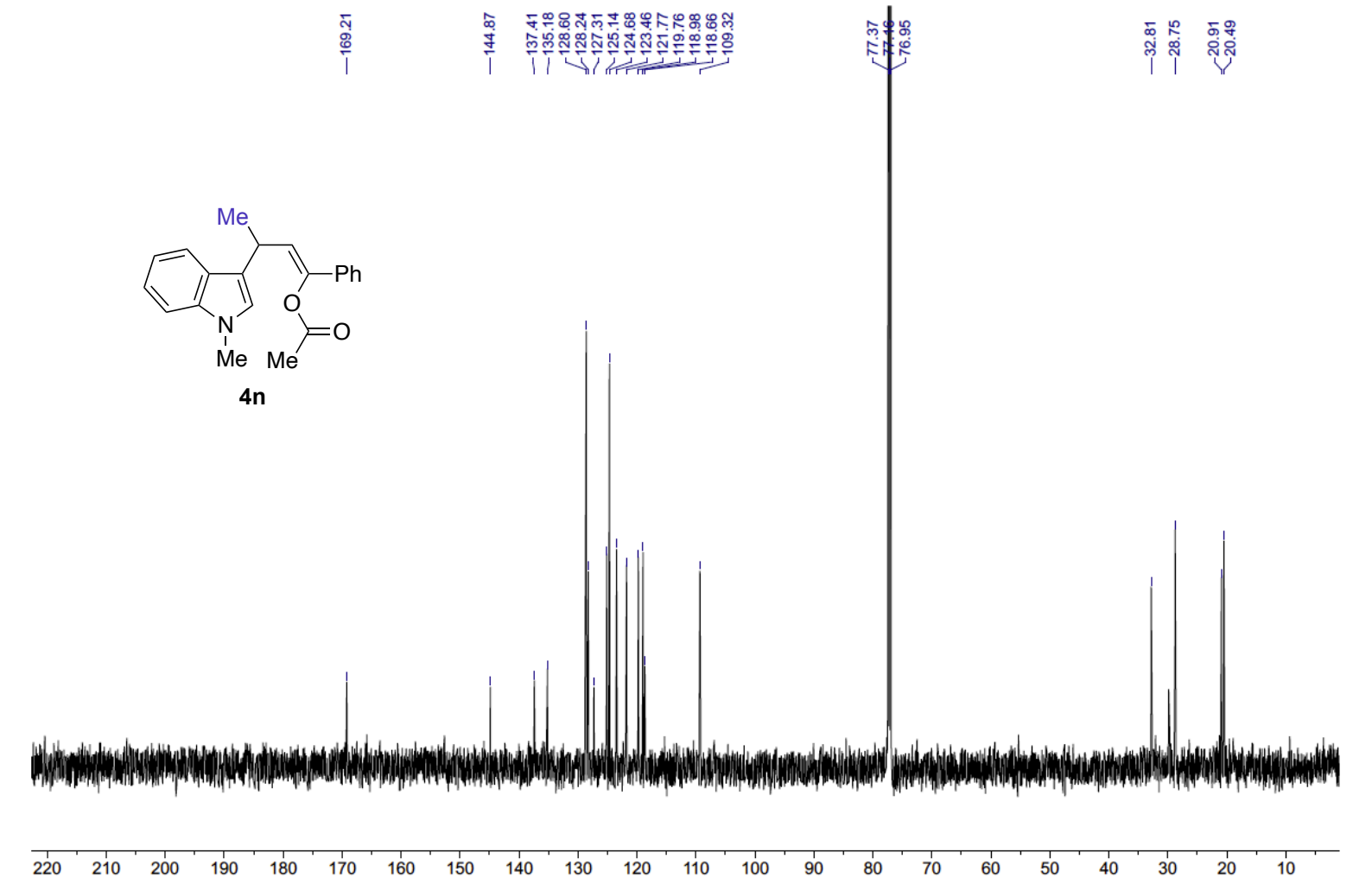

168.55
146.45
137.07
136.77
128.55
128.04
126.21
124.82
124.71
123.84
121.64
121.45
120.64
119.02
111.34
77.37
77.16
76.95
39.82
37.60
26.37
23.06
20.40
Ph
O
N
H
Me
O
4l
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.059
7.728
7.715
7.377
7.374
7.362
7.357
7.345
7.331
7.314
7.311
7.302
7.300
7.289
7.273
7.264
7.261
7.256
7.249
7.173
7.161
7.148
7.076
7.063
7.056
7.052
6.086
3.902
3.895
3.887
3.883
3.875
3.868
3.855
3.850
3.840
3.836
3.831
3.821
3.816
2.364
2.357
2.349
2.341
2.334
2.326
2.319
2.297
2.293
2.287
2.276
2.269
2.264
1.750
O
Ph
O
N
H
O
Me
4m
0.97
1.00
3.09
2.99
1.01
2.00
0.98
4.09
4.00
3.09
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

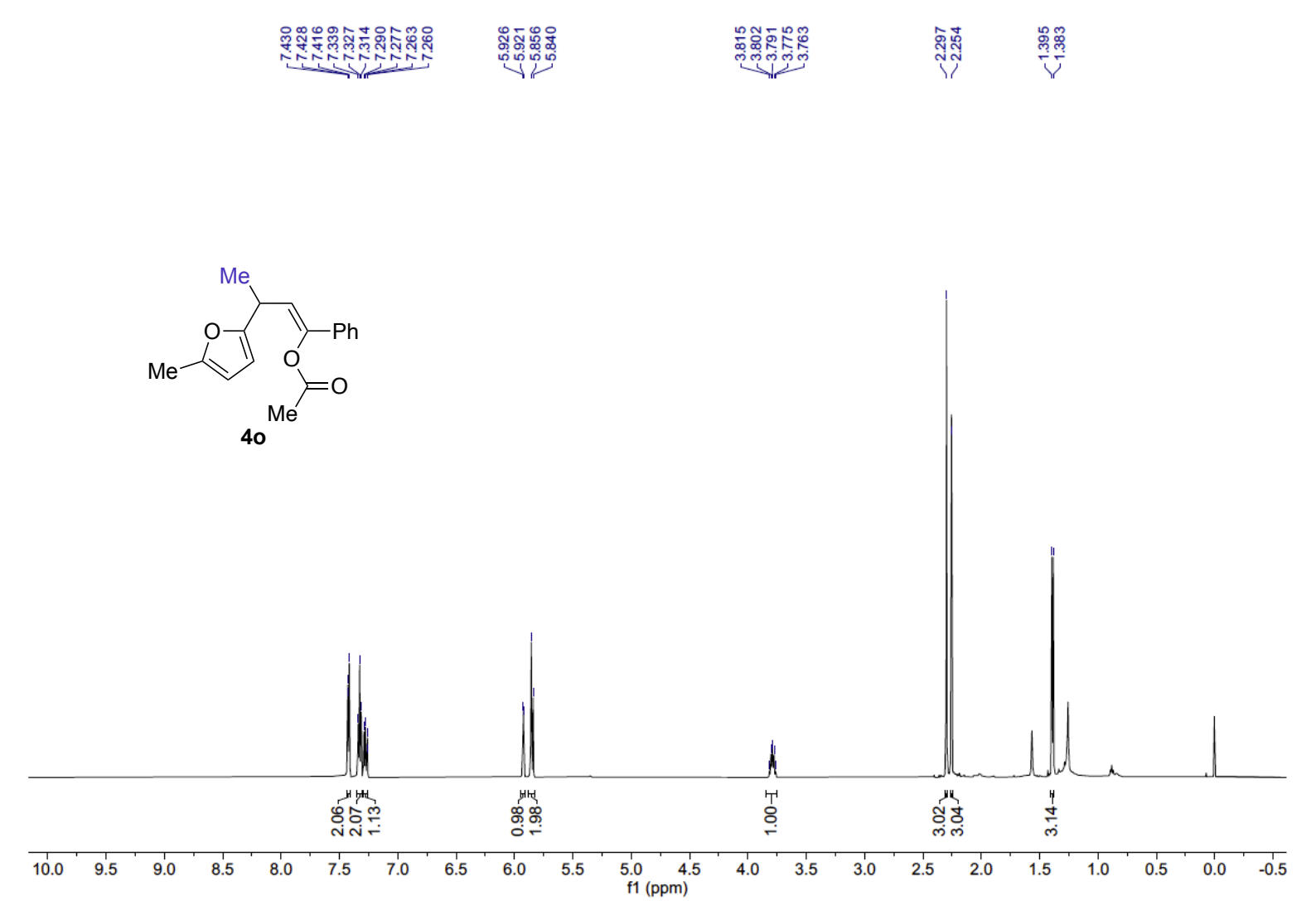

168.33
147.46
137.15
136.39
128.64
128.41
125.91
124.91
123.24
122.14
122.01
121.08
120.82
119.35
111.50
77.37
77.16
76.95
64.87
37.54
37.40
20.45
O
Ph
O
N
H
O
Me
4m
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

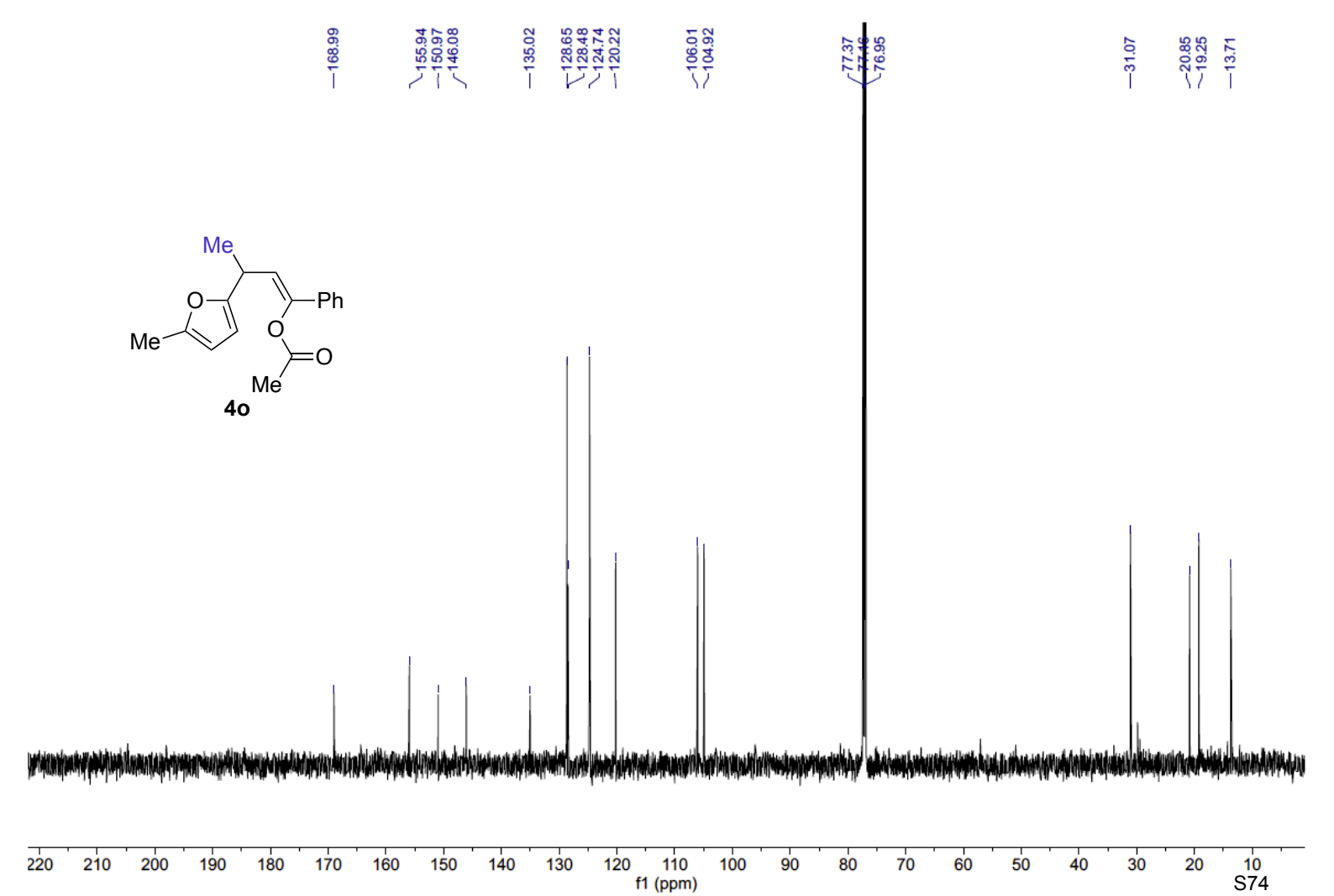

7.714
7.701
7.419
7.404
7.313
7.302
7.294
7.289
7.281
7.262
7.256
7.250
7.237
7.232
7.218
7.207
7.110
7.097
7.085
6.892
5.952
5.936
4.054
4.042
4.025
4.014
4.002
3.754
2.337
1.543
1.532
Me
Ph
O
N
O
Me
Me
0.98
2.04
3.12
1.04
1.06
1.04
1.00
0.98
1.06
3.09
3.00
3.23
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

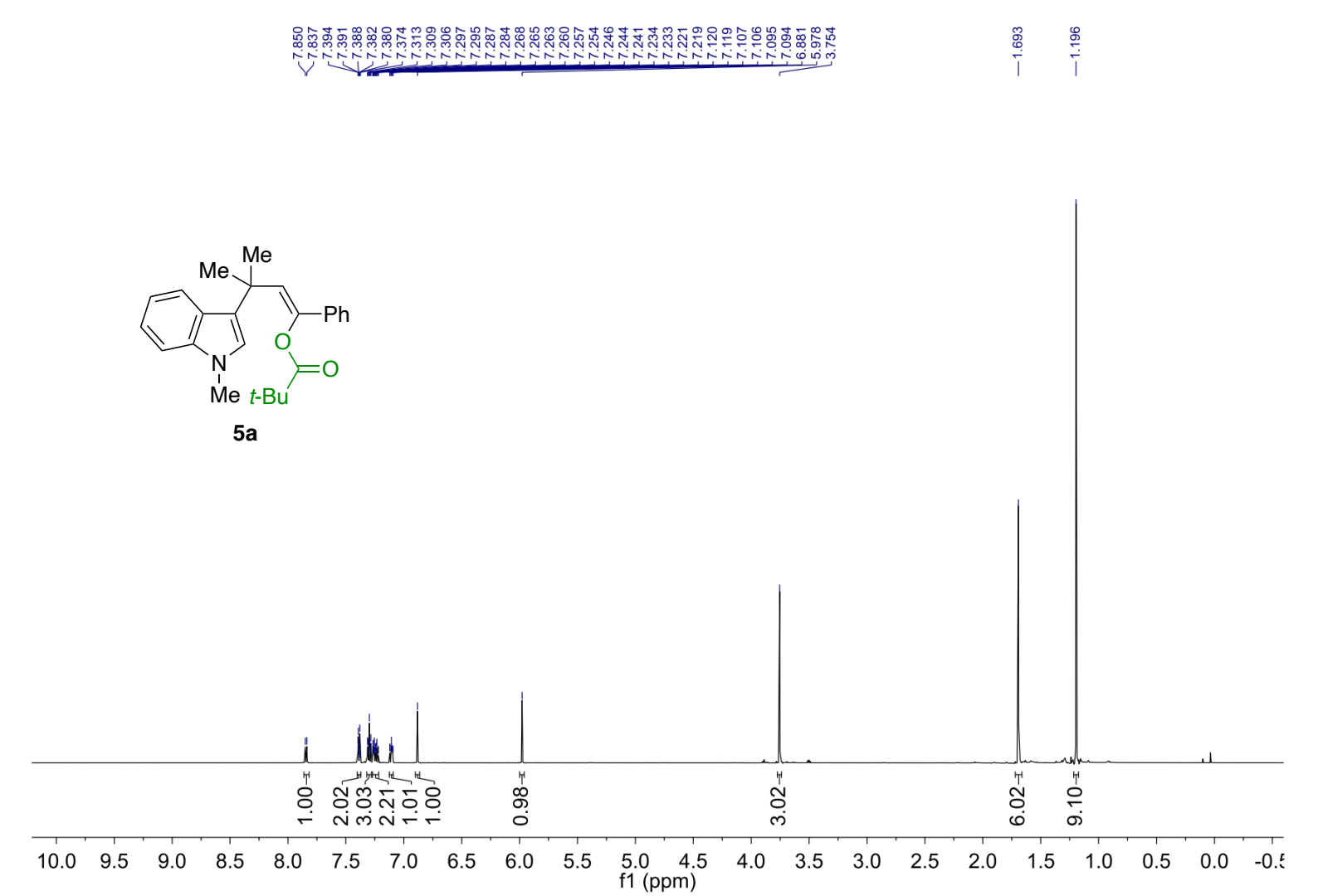
4n


169.21
144.87
137.41
135.18
128.60
128.24
127.31
125.14
124.68
123.46
121.77
119.76
118.98
118.66
109.32
77.37
77.16
76.95
32.81
28.75
20.91
20.49
Me
Ph
O
N
O
Me
Me
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

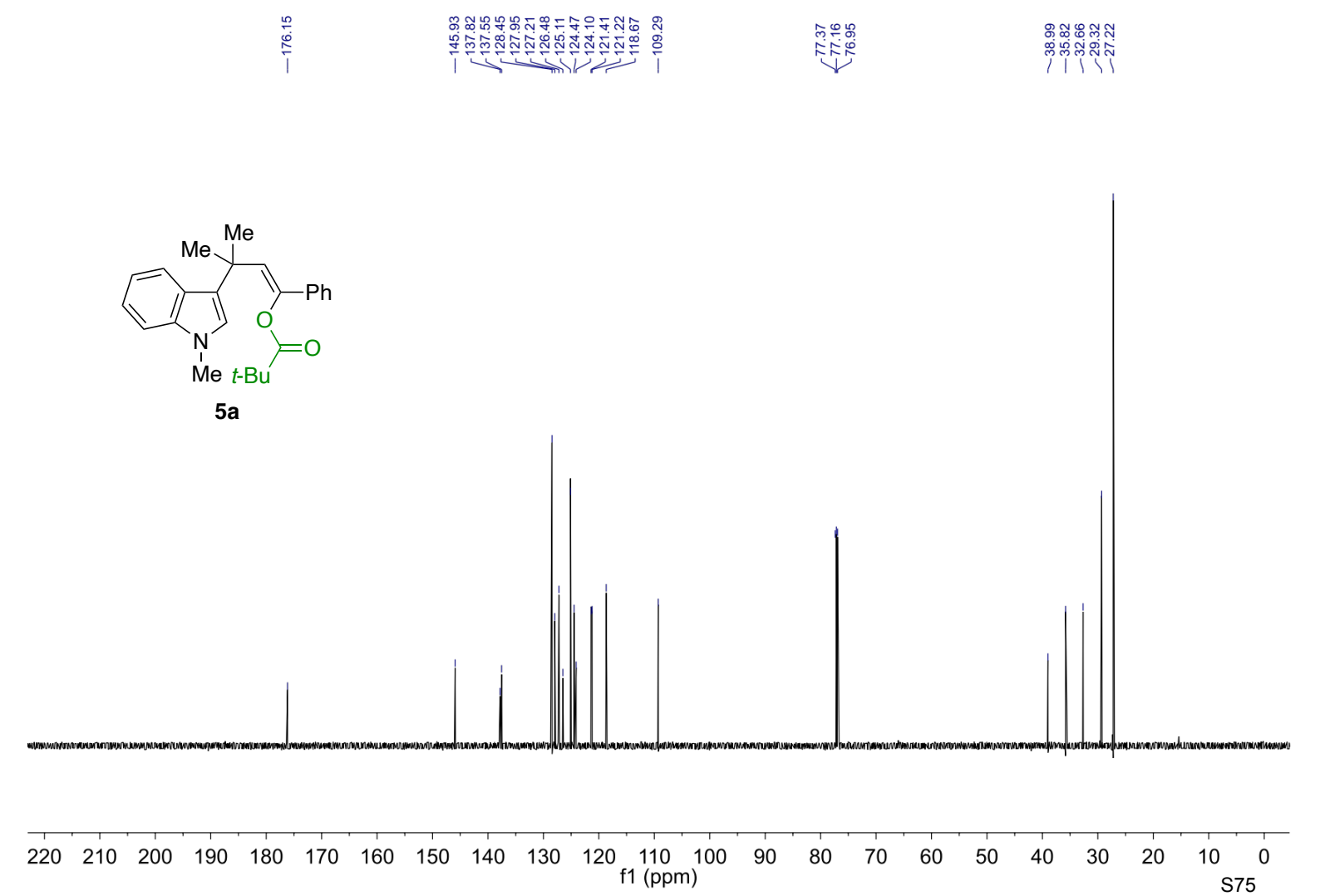
4n


7.430
7.428
7.416
7.339
7.327
7.314
7.290
7.277
7.263
7.260
5.926
5.921
5.856
5.840
3.815
3.802
3.791
3.775
3.763
2.297
2.254
1.395
1.383
Me
O
Ph
Me
O
O
Me
4o
2.06
2.07
1.13
0.98
1.98
1.00
3.02
3.04
3.14
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

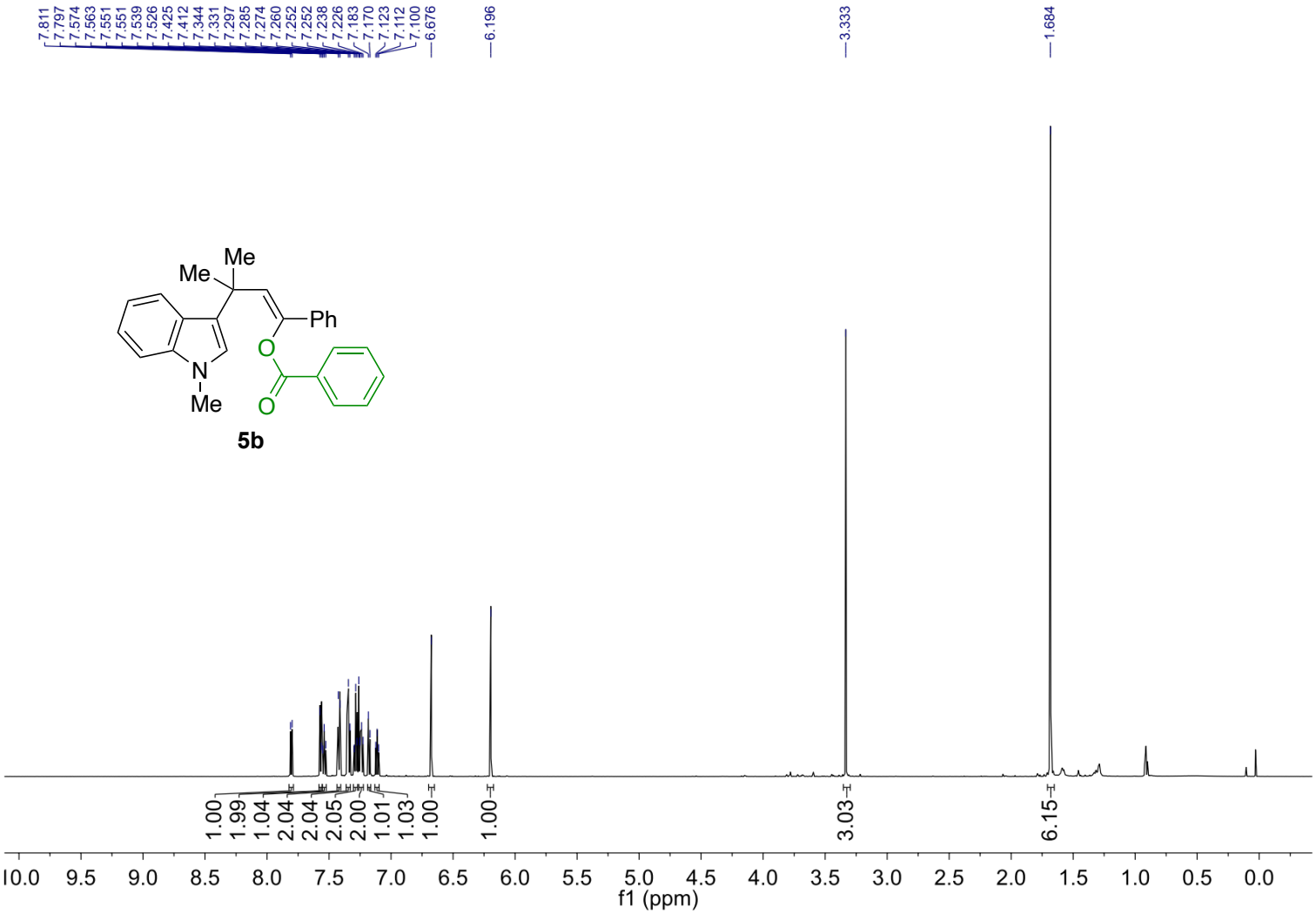

168.99
155.94
150.97
146.08
135.02
128.65
128.48
124.74
120.22
106.01
104.92
77.37
77.16
76.95
31.07
20.85
19.25
13.71
Me
O
Ph
Me
O
O
Me
4o
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

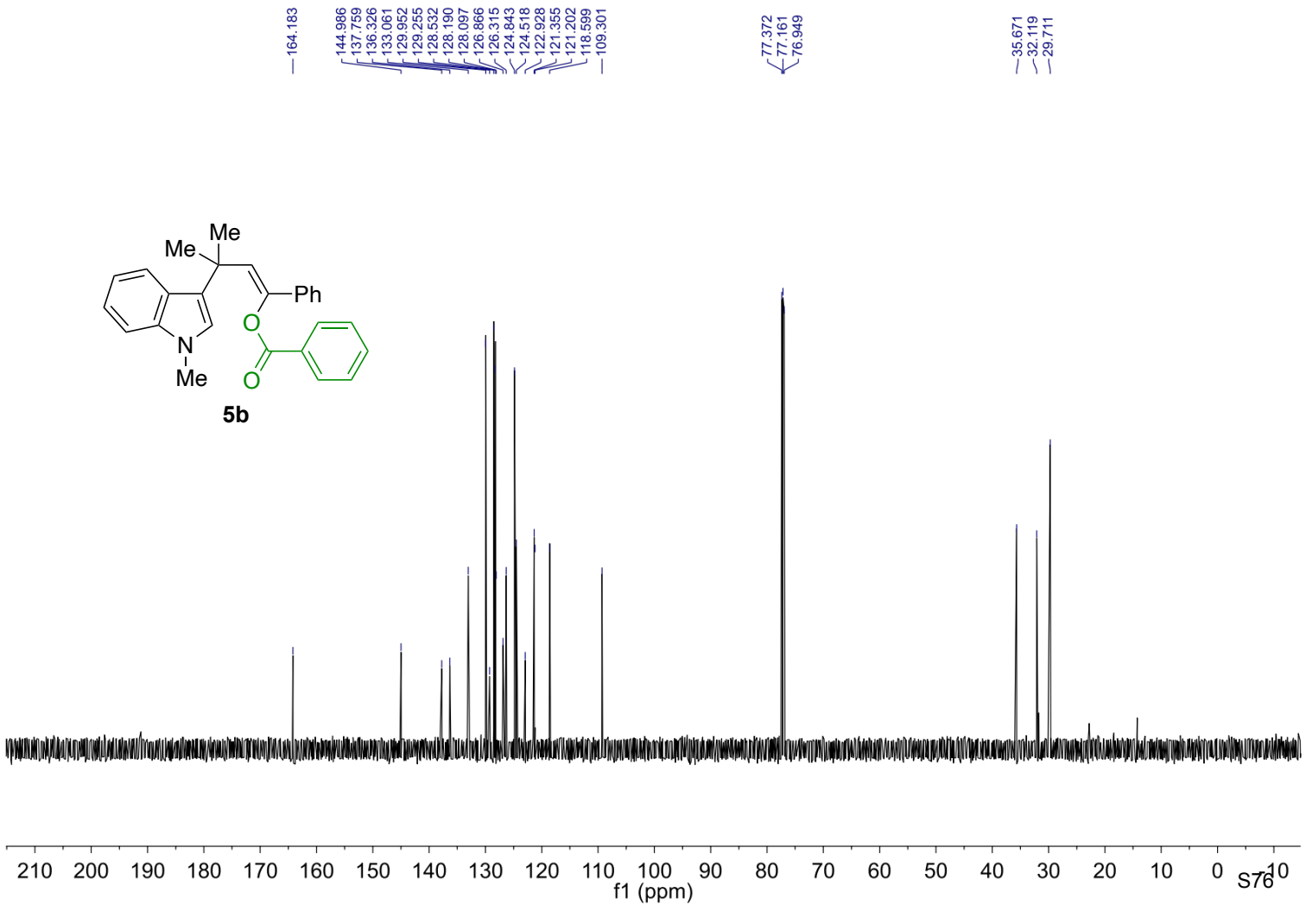

7.850
7.837
7.394
7.391
7.388
7.382
7.380
7.374
7.313
7.309
7.306
7.297
7.295
7.287
7.284
7.268
7.265
7.263
7.260
7.257
7.254
7.246
7.244
7.241
7.234
7.233
7.221
7.219
7.120
7.119
7.107
7.106
7.095
7.094
6.881
5.978
3.754
1.693
1.196
Me
Me
Ph
O
N
Me
t-Bu
O
1.00
2.02
3.03
2.21
1.01
1.00
0.98
3.02
6.02
9.10
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

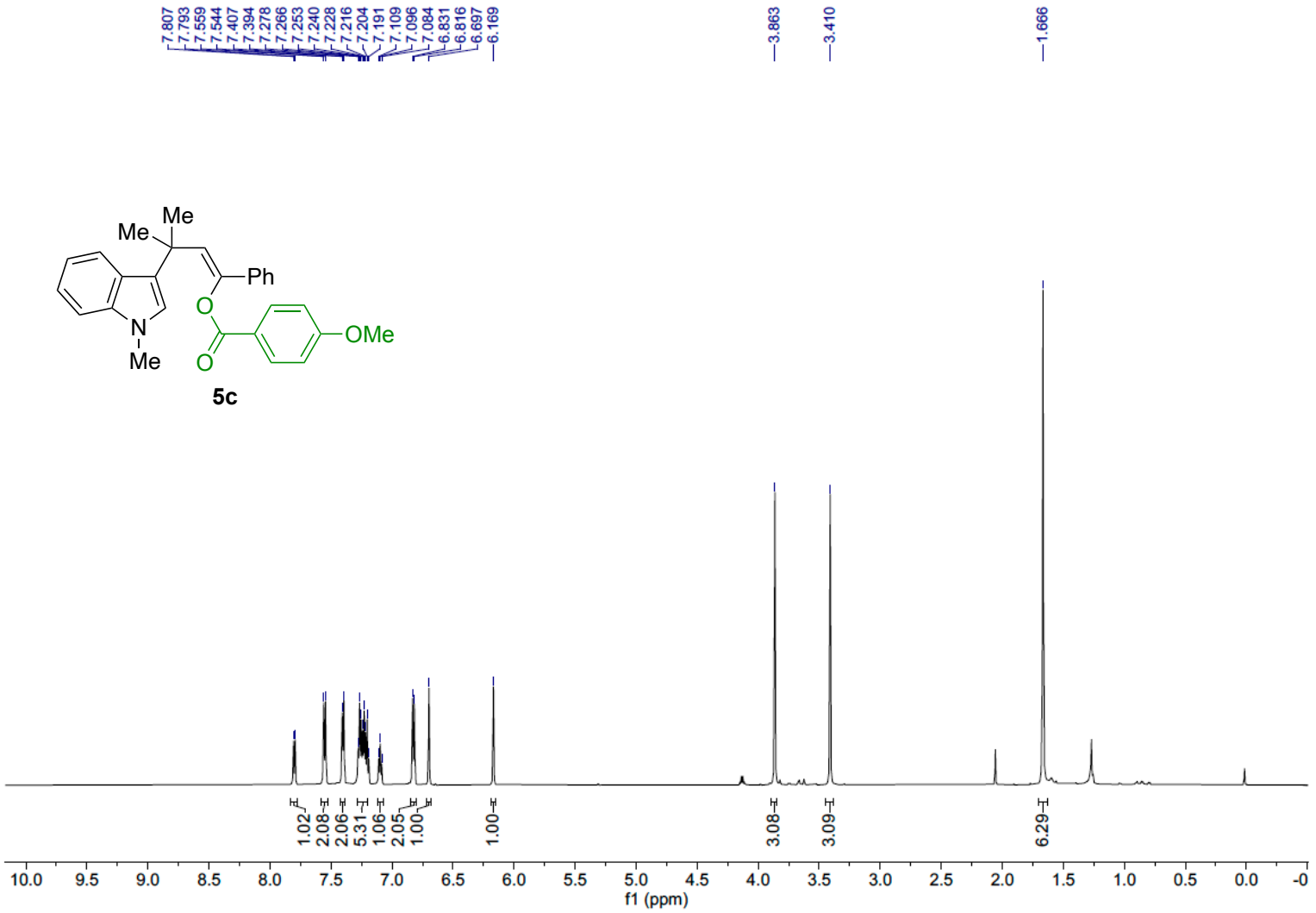
5a

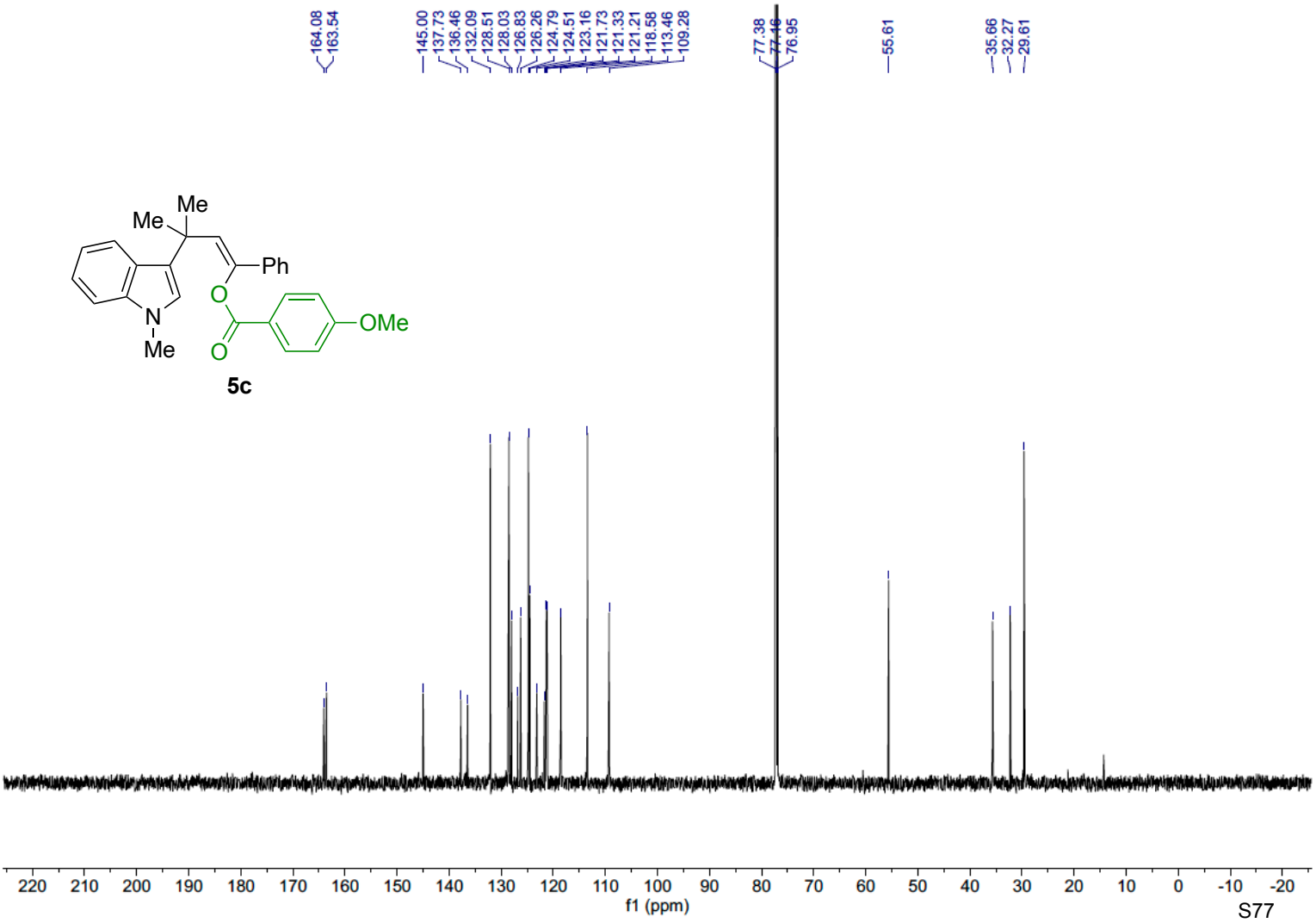

176.15
145.93
137.82
137.55
128.45
127.95
127.21
126.48
125.11
124.47
124.10
121.41
121.22
118.67
109.29
77.37
77.16
76.95
38.99
35.82
32.66
29.32
27.22
Me
Me
Ph
O
N
Me
t-Bu
O
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

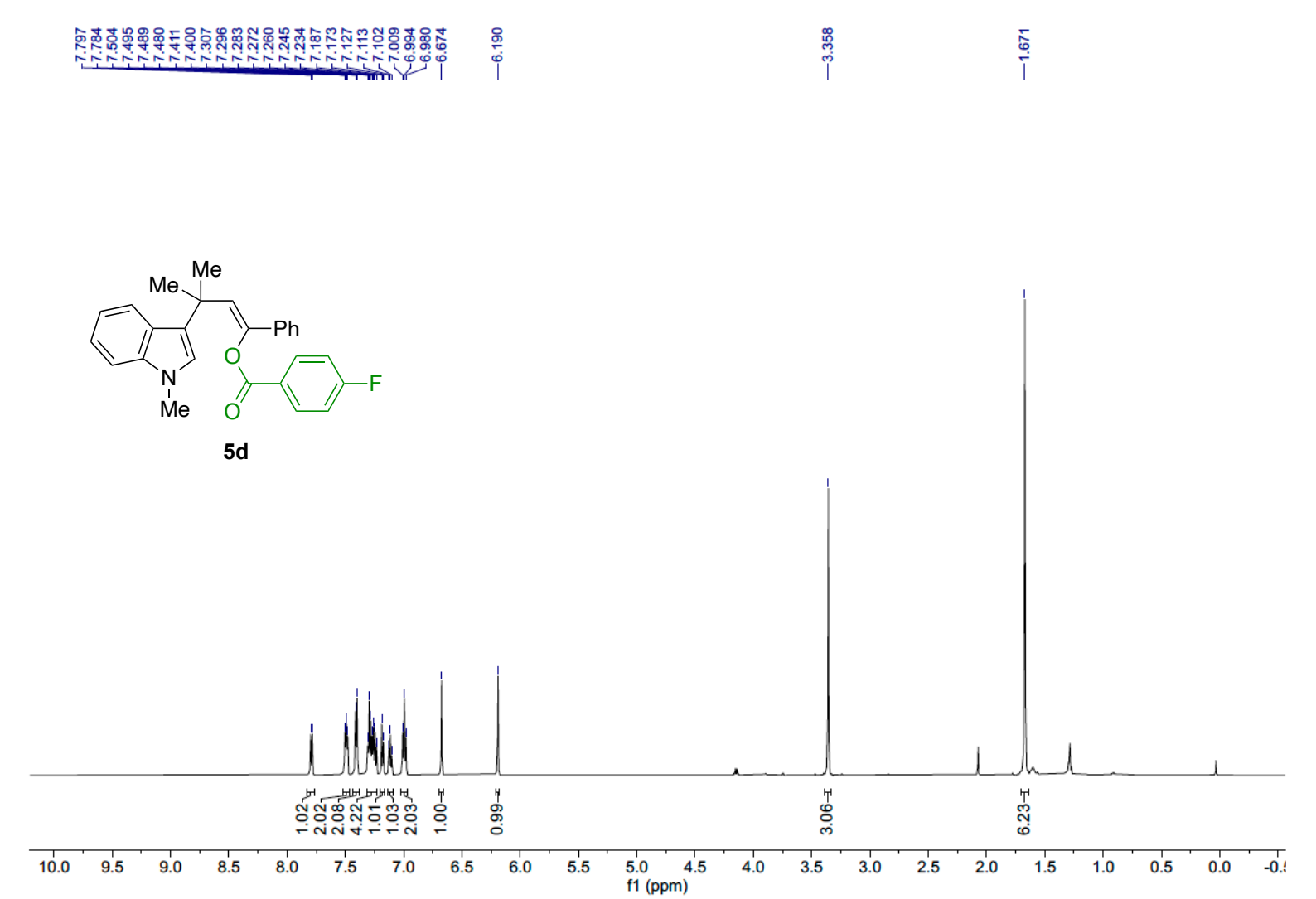
5a


7.811
7.797
7.574
7.563
7.551
7.551
7.539
7.526
7.425
7.412
7.344
7.331
7.297
7.285
7.274
7.260
7.252
7.252
7.238
7.226
7.183
7.170
7.123
7.112
7.100
6.676
6.196
3.333
1.684
Me
Me
Ph
O
N
Me
O
5b
1.00
1.99
1.04
2.04
2.04
2.05
2.00
1.01
1.03
1.00
1.00
3.03
6.15
f1 (ppm)

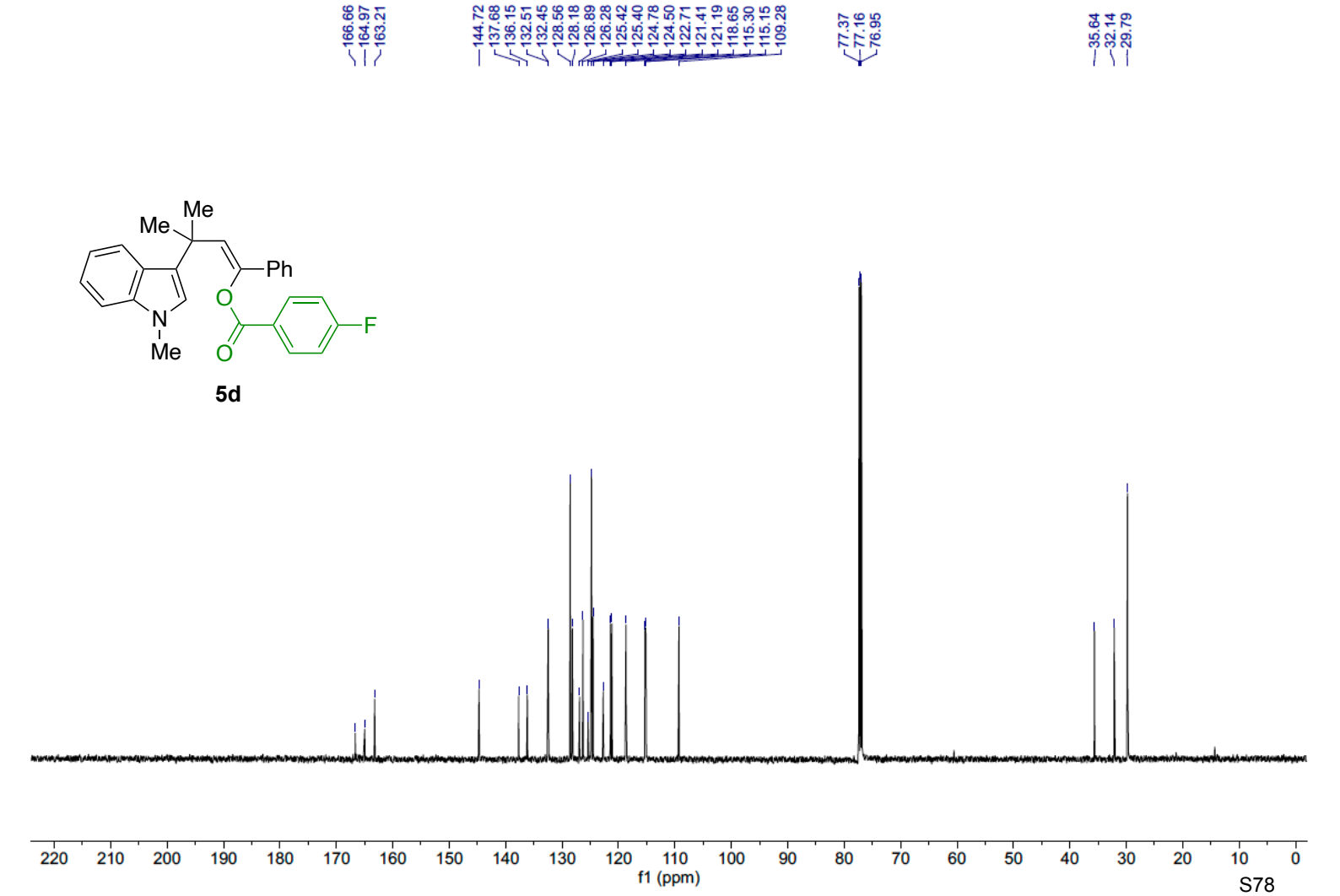

164.183
144.986
137.759
136.326
133.061
129.952
129.255
128.532
128.190
128.097
126.866
126.315
124.843
124.518
122.928
121.355
121.202
118.599
109.301
77.372
77.161
76.949
35.671
32.119
29.711
Me
Me
Ph
O
N
Me
O
5b
f1 (ppm)


7.807
7.793
7.559
7.544
7.407
7.394
7.278
7.266
7.253
7.240
7.228
7.216
7.204
7.191
7.109
7.096
7.084
6.831
6.816
6.697
6.169
3.863
3.410
1.666
Me
Me
Ph
O
N
Me
O
OMe
O
5c
1.02
2.08
2.06
5.31
1.06
2.05
1.00
1.00
3.08
3.09
6.29
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)

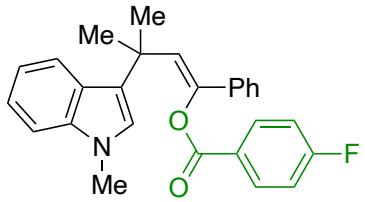

164.08
163.54
145.00
137.73
136.46
132.09
128.51
128.03
126.83
126.26
124.79
124.51
123.16
121.73
121.33
121.21
118.58
113.46
109.28
77.38
77.16
76.95
55.61
35.66
32.27
29.61
Me
Me
Ph
O
N
Me
O
OMe
O
5c
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)


7.797
7.784
7.504
7.495
7.489
7.480
7.411
7.400
7.307
7.296
7.283
7.272
7.260
7.245
7.234
7.187
7.173
7.127
7.113
7.102
7.009
6.994
6.980
6.674
6.190
3.358
1.671
Me
Me
Ph
O
N
Me
O
F
1.02
2.02
2.08
4.22
1.01
1.03
2.03
1.00
0.99
3.06
6.23
f1 (ppm)

5d


166.66
164.97
163.21
144.72
137.68
136.15
132.51
132.45
128.56
128.18
126.89
126.28
125.42
125.40
124.78
124.50
122.71
121.41
121.19
118.65
115.30
115.15
109.28
77.37
77.16
76.95
35.64
32.14
29.79
Me
Me
Ph
O
N
Me
O
F
f1 (ppm)

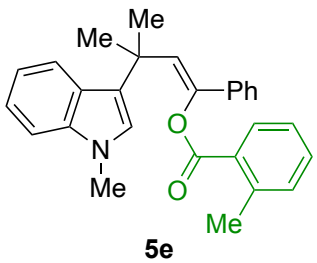
5d


Me
Me
Ph
O
N
Me
O
F

5d

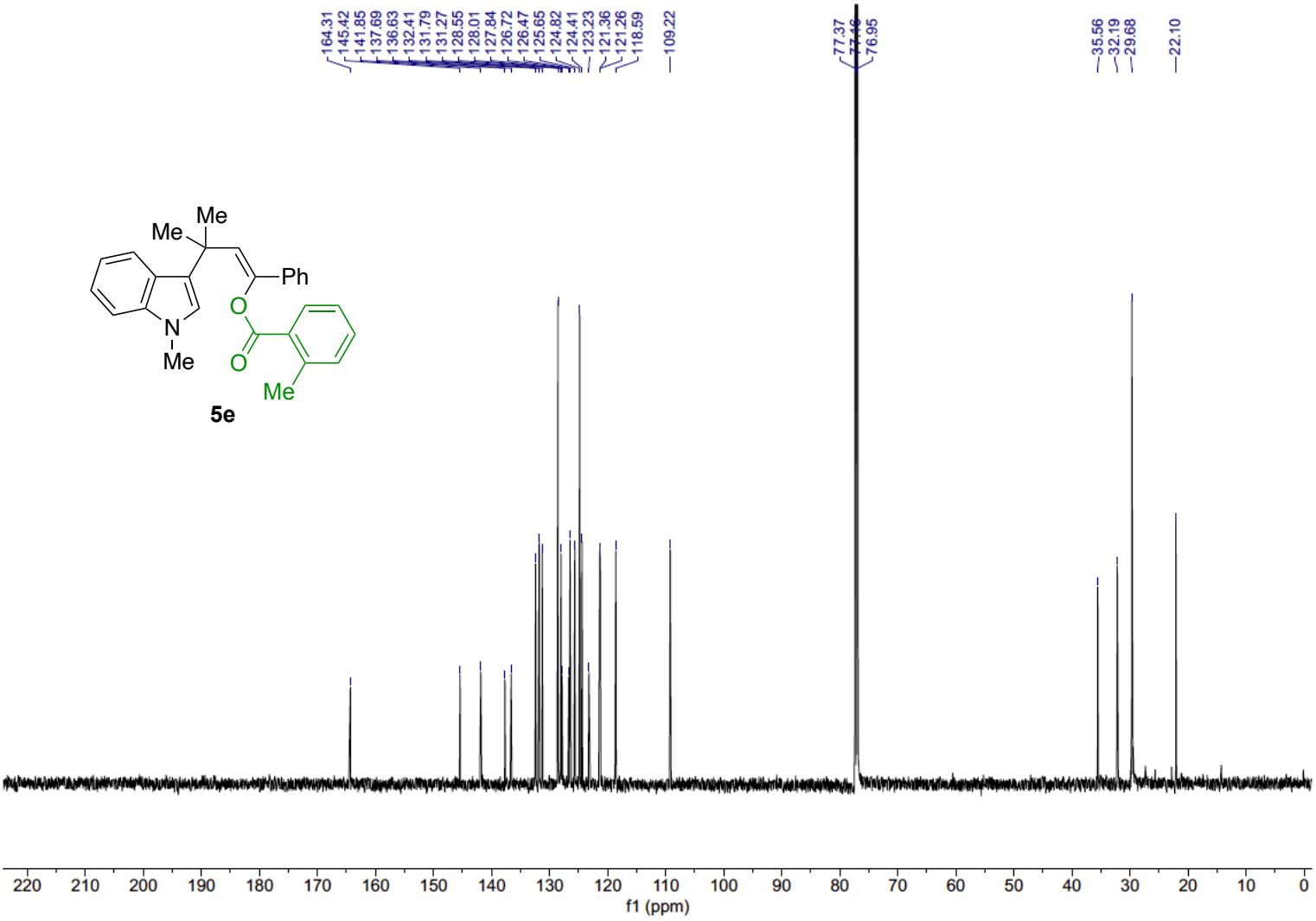
-105.29
40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240
f1 (ppm)


7.798
7.784
7.525
7.511
7.438
7.426
7.406
7.396
7.384
7.295
7.284
7.271
7.260
7.252
7.240
7.216
7.205
7.191
7.170
7.156
7.148
7.136
7.098
7.085
6.879
6.179
3.385
2.403
1.679

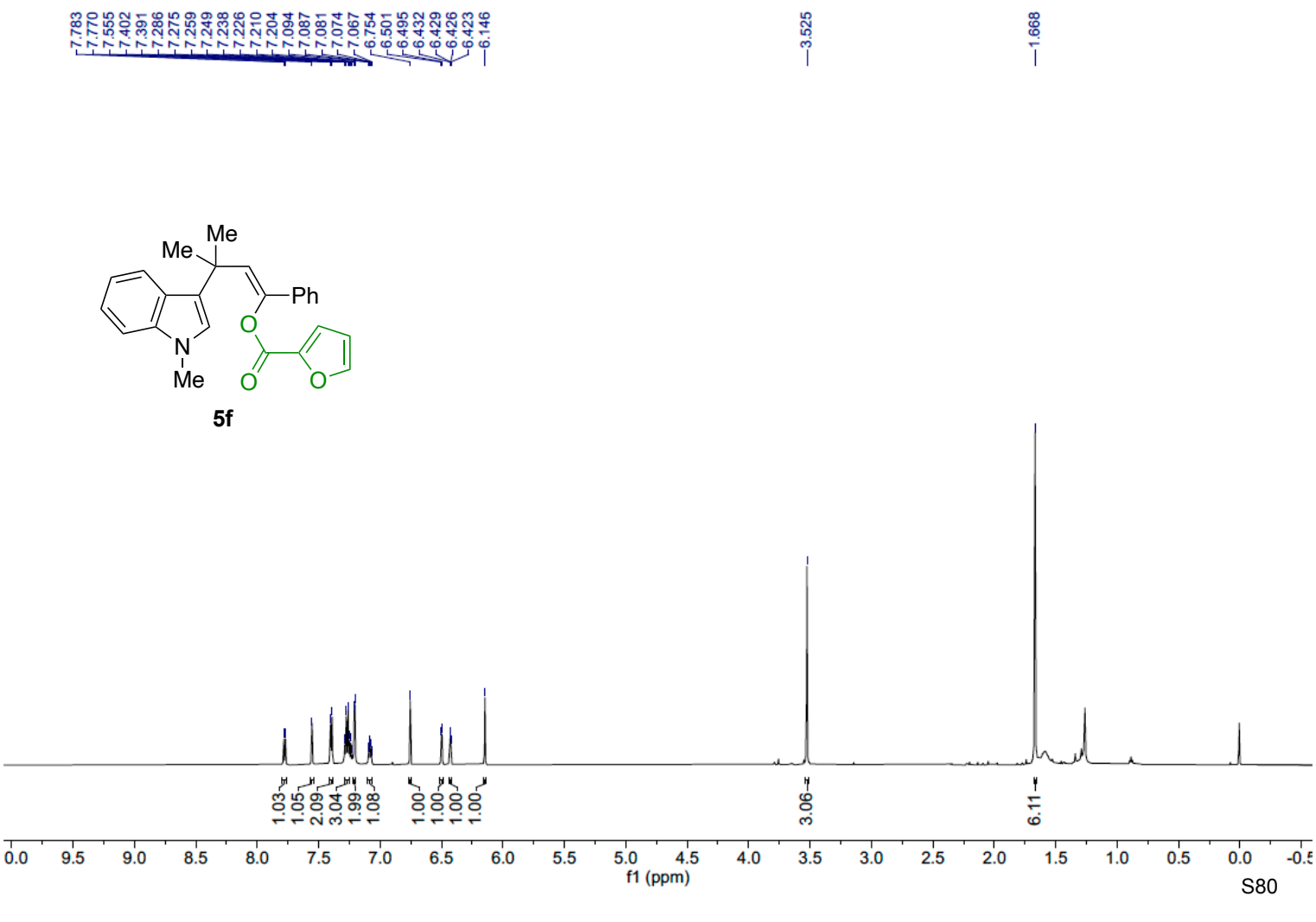

Me
Me
Ph
O
N
Me
O
Me

5e

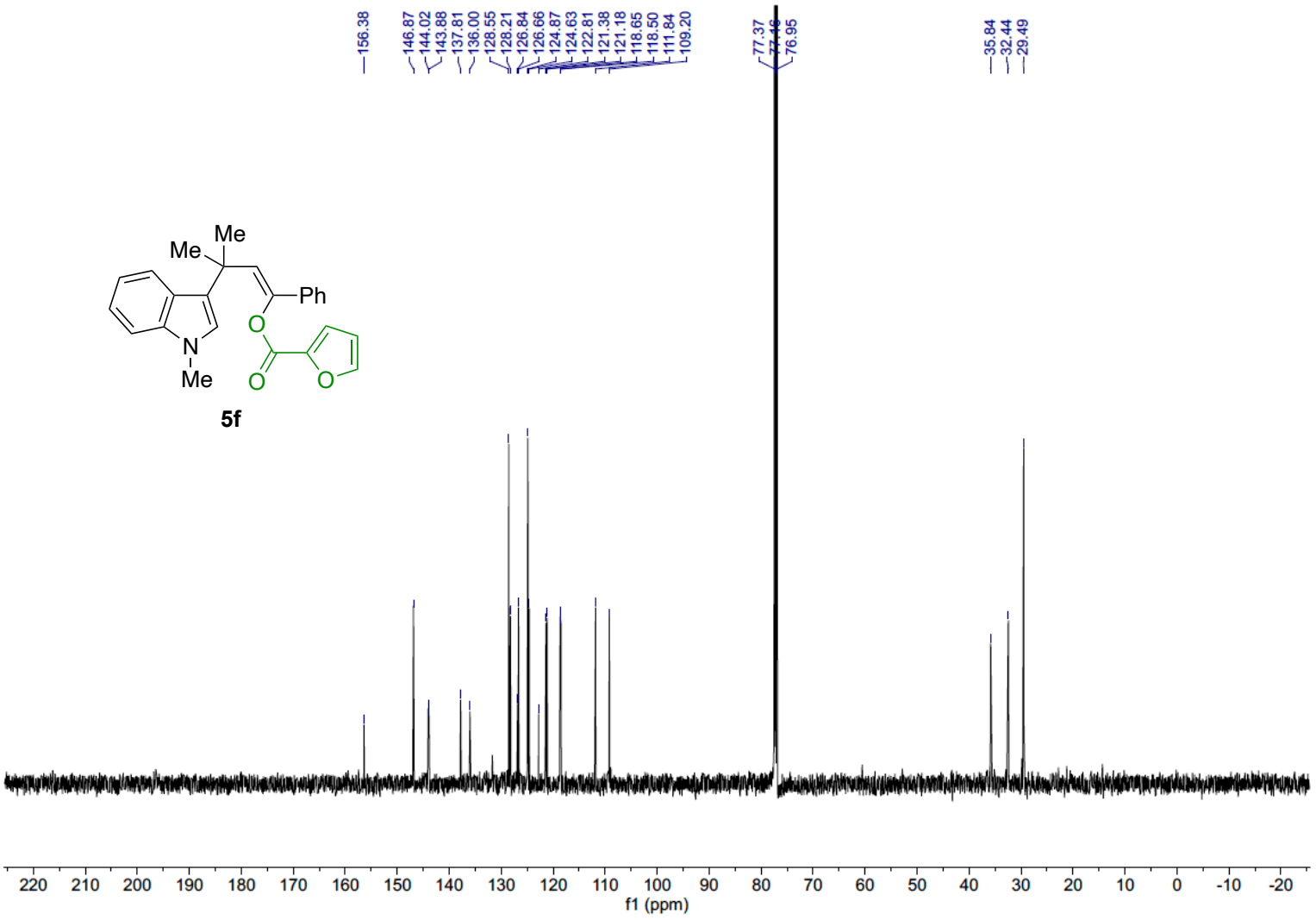
1.01
1.00
2.02
1.04
3.08
4.03
1.01
1.00
0.99
3.07
3.06
6.11
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


164.31
145.42
141.85
137.69
136.63
132.41
131.79
131.27
128.55
128.01
127.84
126.72
126.47
125.65
124.82
124.41
123.23
121.36
121.26
118.59
109.22
77.37
77.16
76.95
35.56
32.19
29.68
22.10
Me
Me
Ph
O
N
Me
O
Me
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

5e


7.783
7.770
7.555
7.402
7.391
7.286
7.275
7.259
7.249
7.238
7.226
7.210
7.204
7.094
7.087
7.081
7.074
7.067
6.754
6.501
6.495
6.432
6.429
6.426
6.423
6.146
3.525
1.668
Me
Me
Ph
O
N
Me
O
O
1.03
1.05
2.09
3.04
1.99
1.08
1.00
1.00
1.00
1.00
3.06
6.11
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

5f

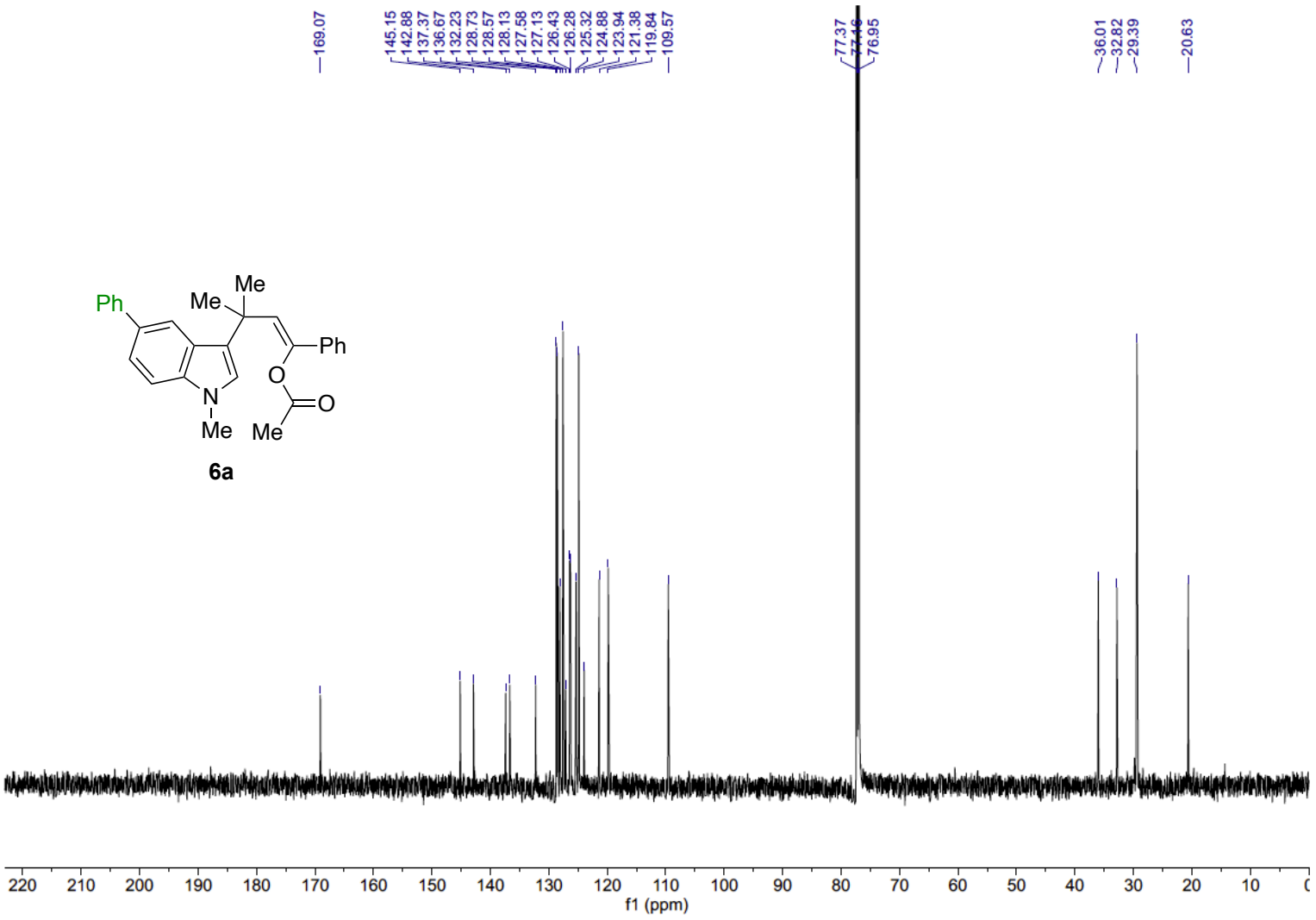

156.38
146.87
144.02
143.88
137.81
136.00
128.55
128.21
126.84
126.66
124.87
124.63
122.81
121.38
121.18
118.65
118.50
111.84
109.20
77.37
77.16
76.95
35.84
32.44
29.49
Me
Me
Ph
O
N
Me
O
O
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

5f

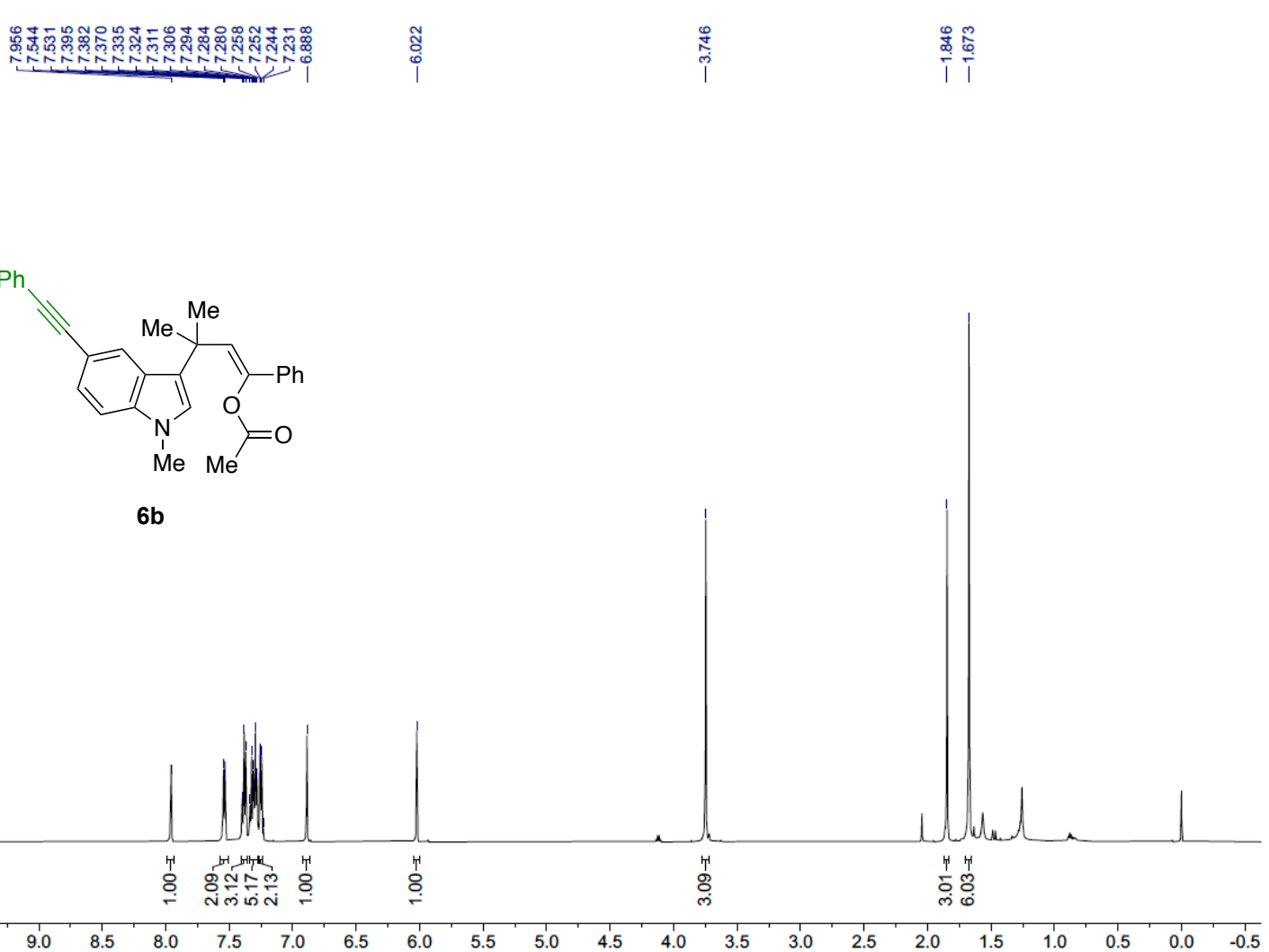

8.006
7.630
7.616
7.483
7.469
7.419
7.407
7.393
7.379
7.357
7.343
7.306
7.292
7.281
7.271
7.260
7.246
7.233
6.902
6.008
3.779
1.905
1.698
1.01
2.03
1.06
4.12
1.07
3.07
0.99
0.96
0.98
3.00
3.06
6.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

Ph
Me
Me
Ph
O
N
Me
Me
O

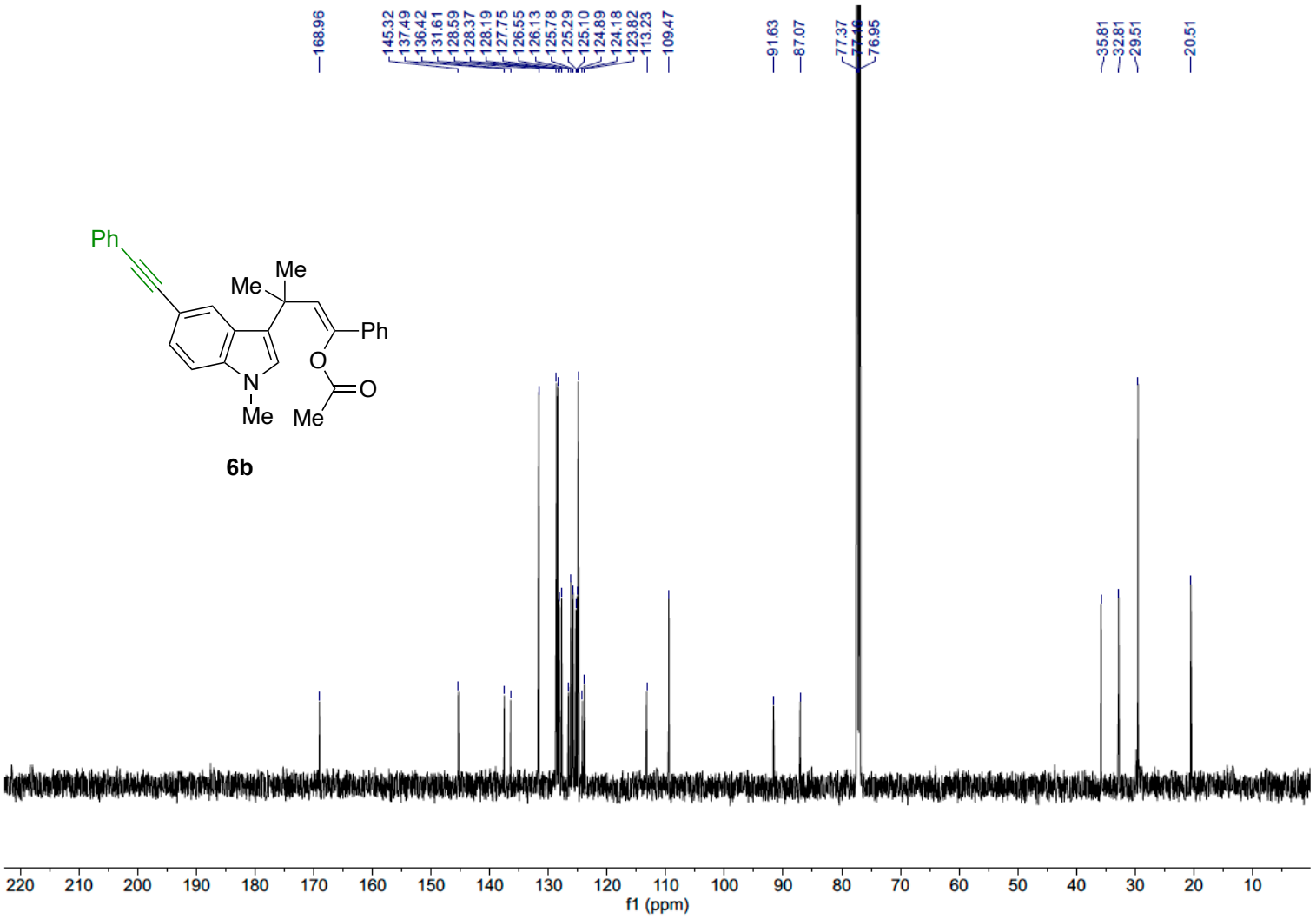
6a


169.07
145.15
142.88
137.37
136.67
132.23
128.73
128.57
128.13
127.58
127.13
126.43
126.28
125.32
124.88
123.94
121.38
119.84
109.57
77.37
77.16
76.95
36.01
32.82
29.39
20.63
Ph
Me
Me
Ph
O
O
N
Me
Me
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

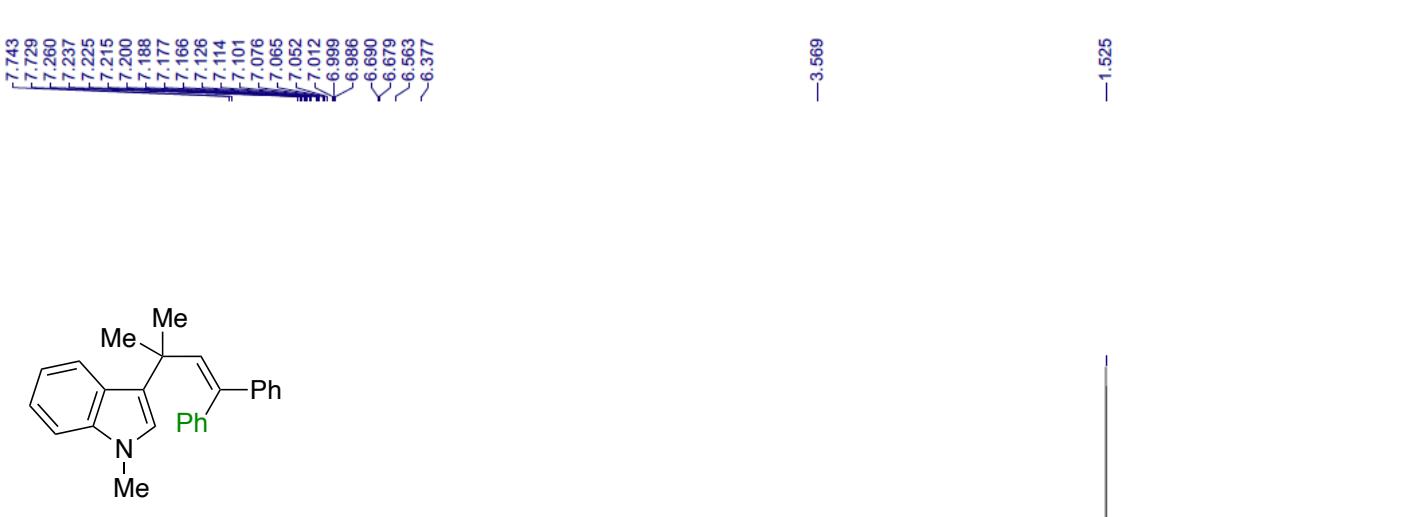
6a


7.956
7.544
7.531
7.395
7.382
7.370
7.335
7.324
7.311
7.306
7.294
7.284
7.280
7.258
7.252
7.244
7.231
6.888
6.022
3.746
1.846
1.673
Ph
Me
Me
Ph
O
O
N
Me
Me
1.00
2.09
3.12
5.17
2.13
1.00
1.00
3.09
3.01
6.03
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

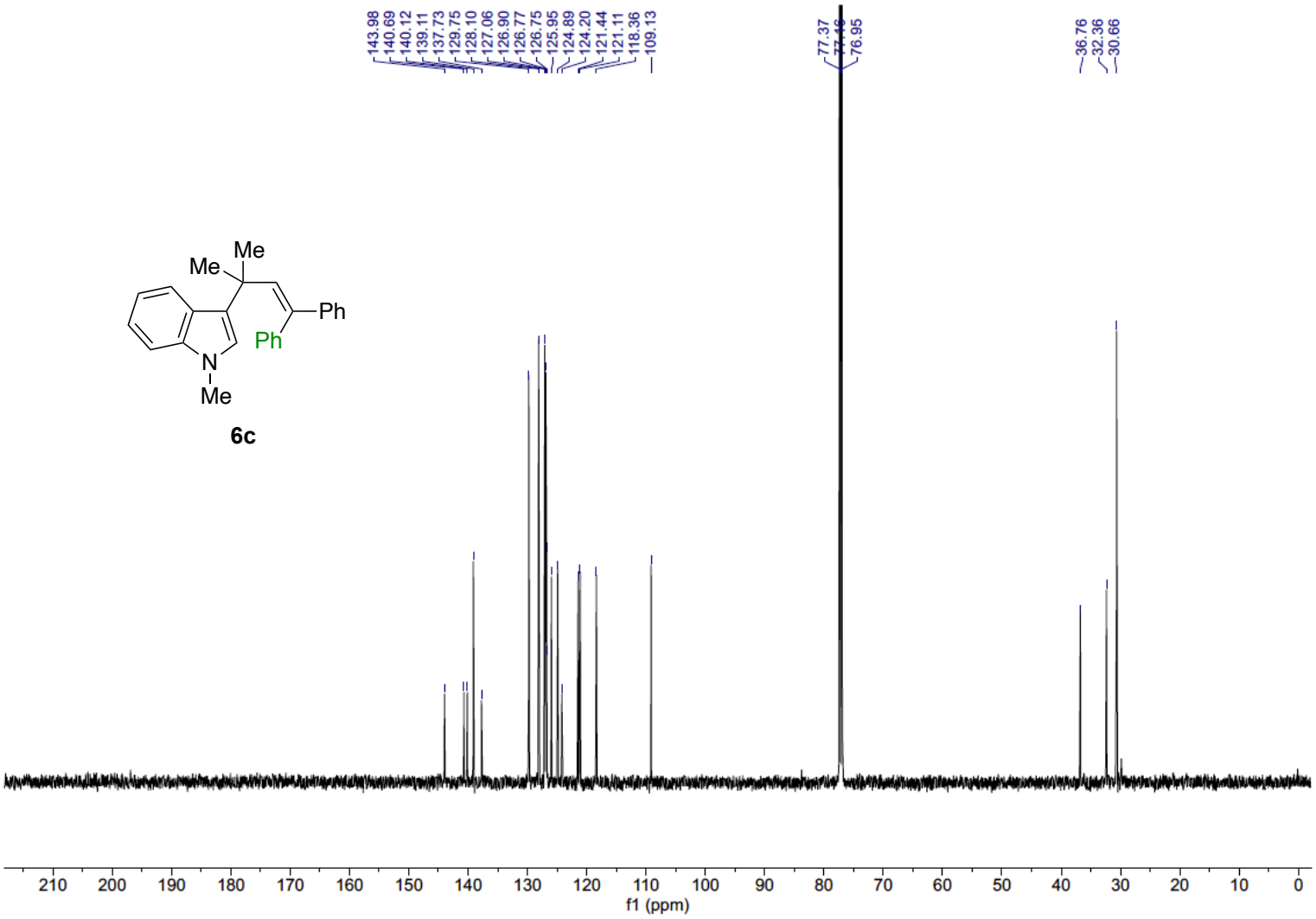
6b


168.96
145.32
137.49
136.42
131.61
128.59
128.37
128.19
127.75
126.55
126.13
125.78
125.29
125.10
124.89
124.18
123.82
113.23
109.47
91.63
87.07
77.37
77.16
76.95
35.81
32.81
29.51
20.51
Ph
Me
Me
Ph
O
O
N
Me
Me
f1 (ppm)

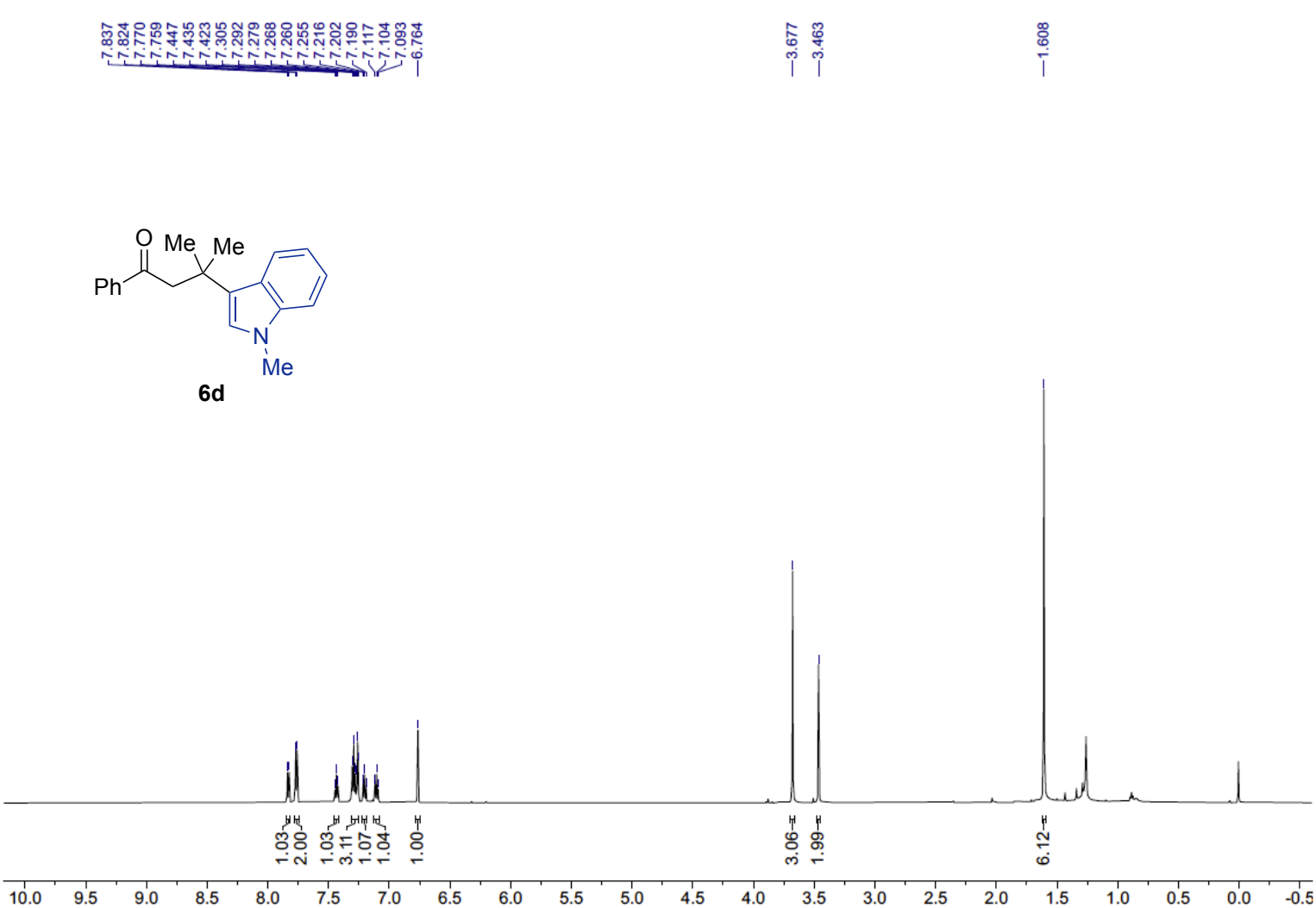
6b


7.743
7.729
7.260
7.237
7.225
7.215
7.200
7.188
7.177
7.166
7.126
7.114
7.101
7.076
7.065
7.052
7.012
6.999
6.986
6.690
6.679
6.563
6.377
3.569
1.525
Me
Me
Ph
Ph
N
Me
1.00
7.00
1.02
1.01
2.01
2.00
1.00
0.99
3.05
6.08
f1 (ppm)

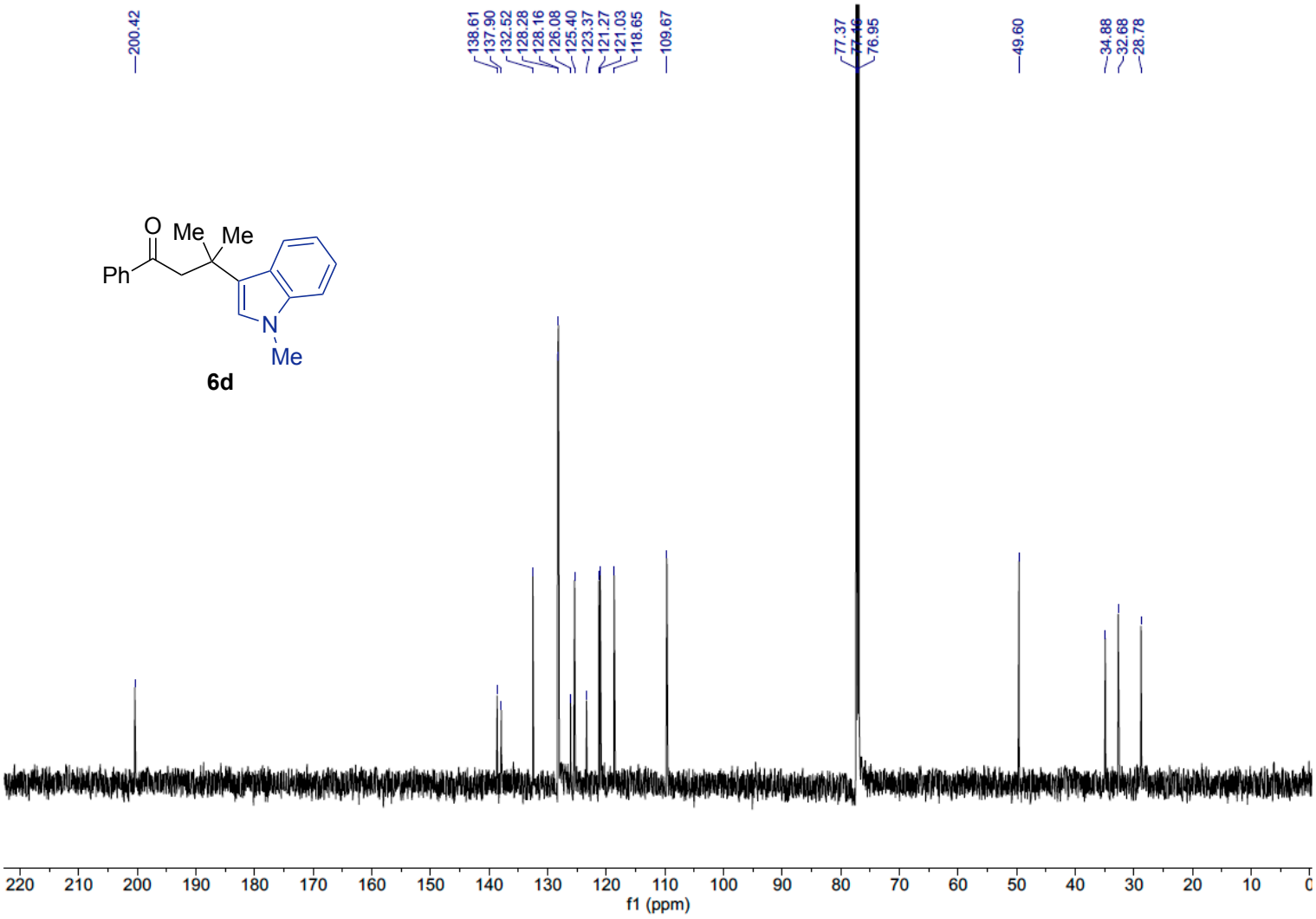
6c

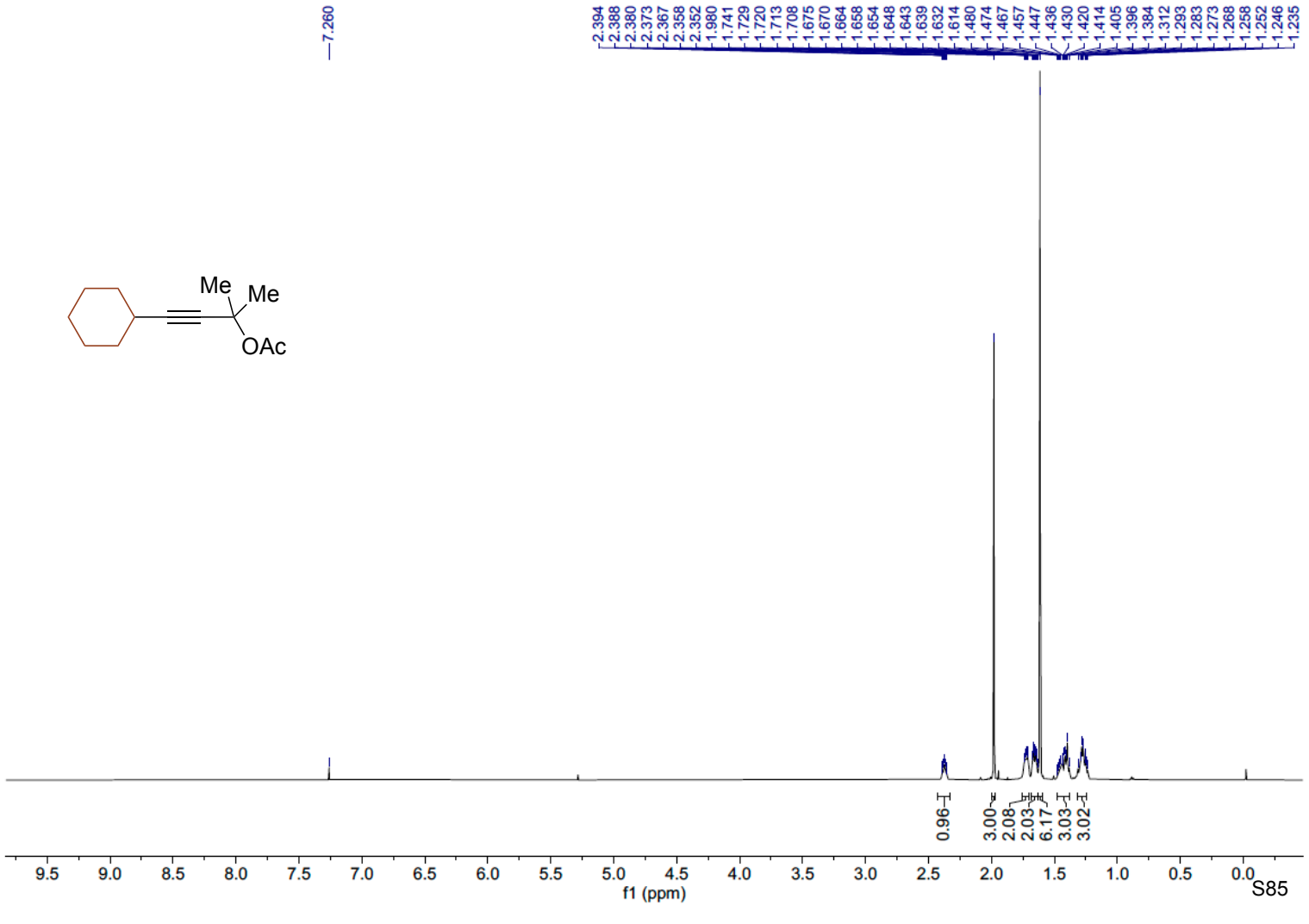

143.98
140.69
140.12
139.11
137.73
129.75
128.10
127.06
126.90
126.77
126.75
125.95
124.89
124.20
121.44
121.11
118.36
109.13
77.37
77.46
76.95
36.76
32.36
30.66
Me
Me
Ph
Ph
N
Me
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

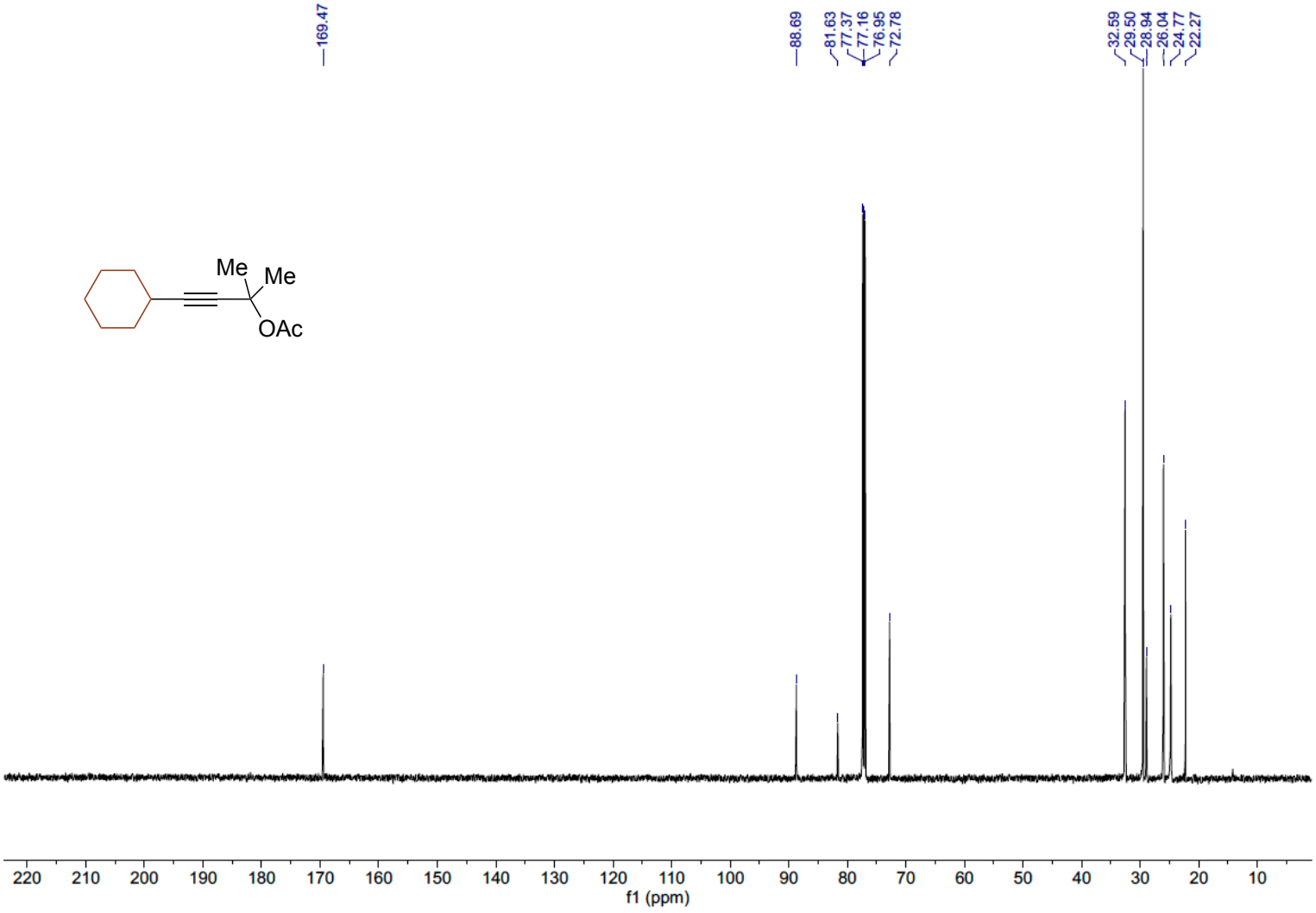
6c

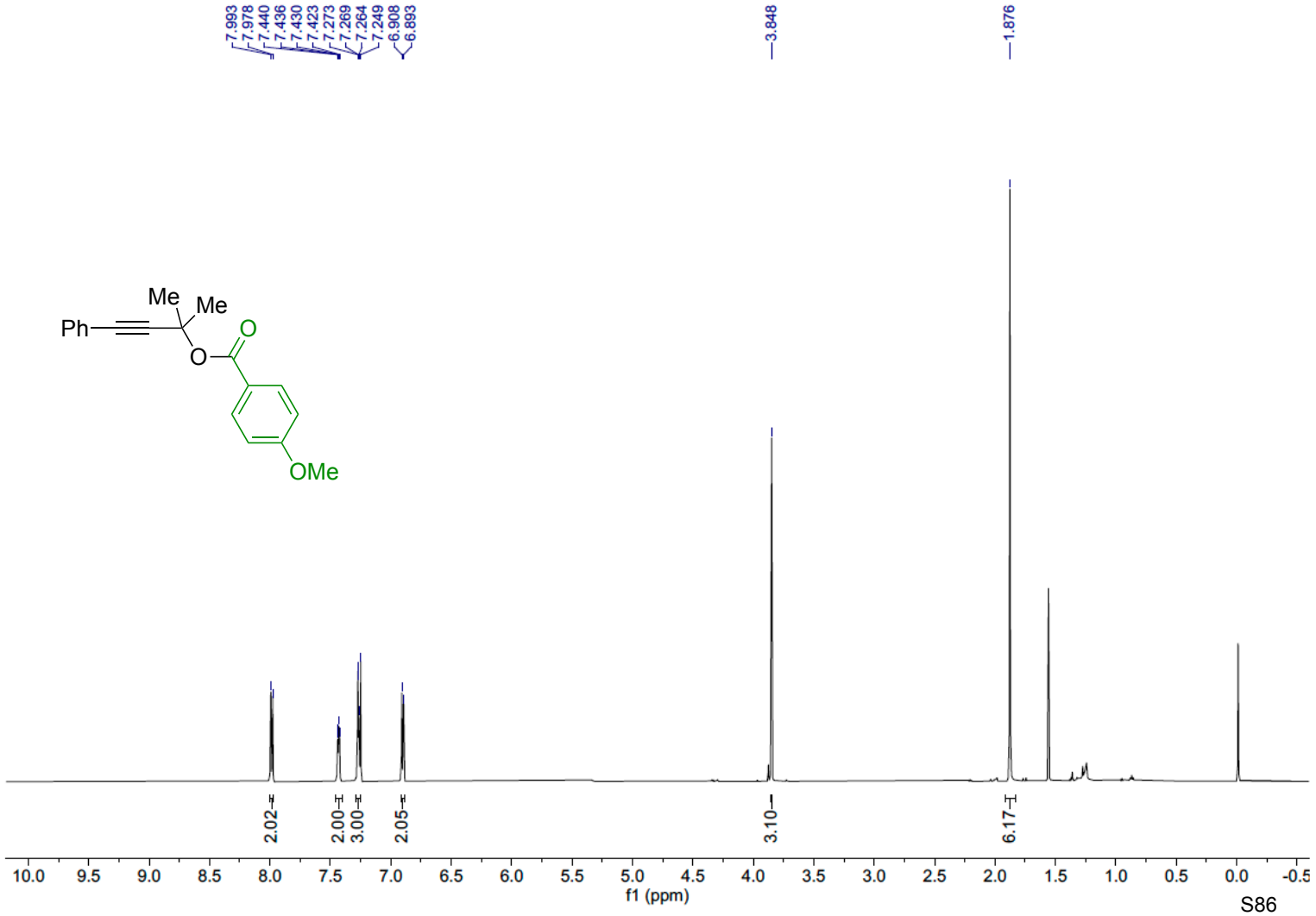

7.837
7.824
7.770
7.759
7.447
7.435
7.423
7.305
7.292
7.279
7.268
7.260
7.255
7.216
7.202
7.190
7.117
7.104
7.093
6.764
3.677
3.463
1.608
O
Me
Me
Ph
N
Me
1.03
2.00
1.03
3.11
1.07
1.04
1.00
3.06
1.99
6.12
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

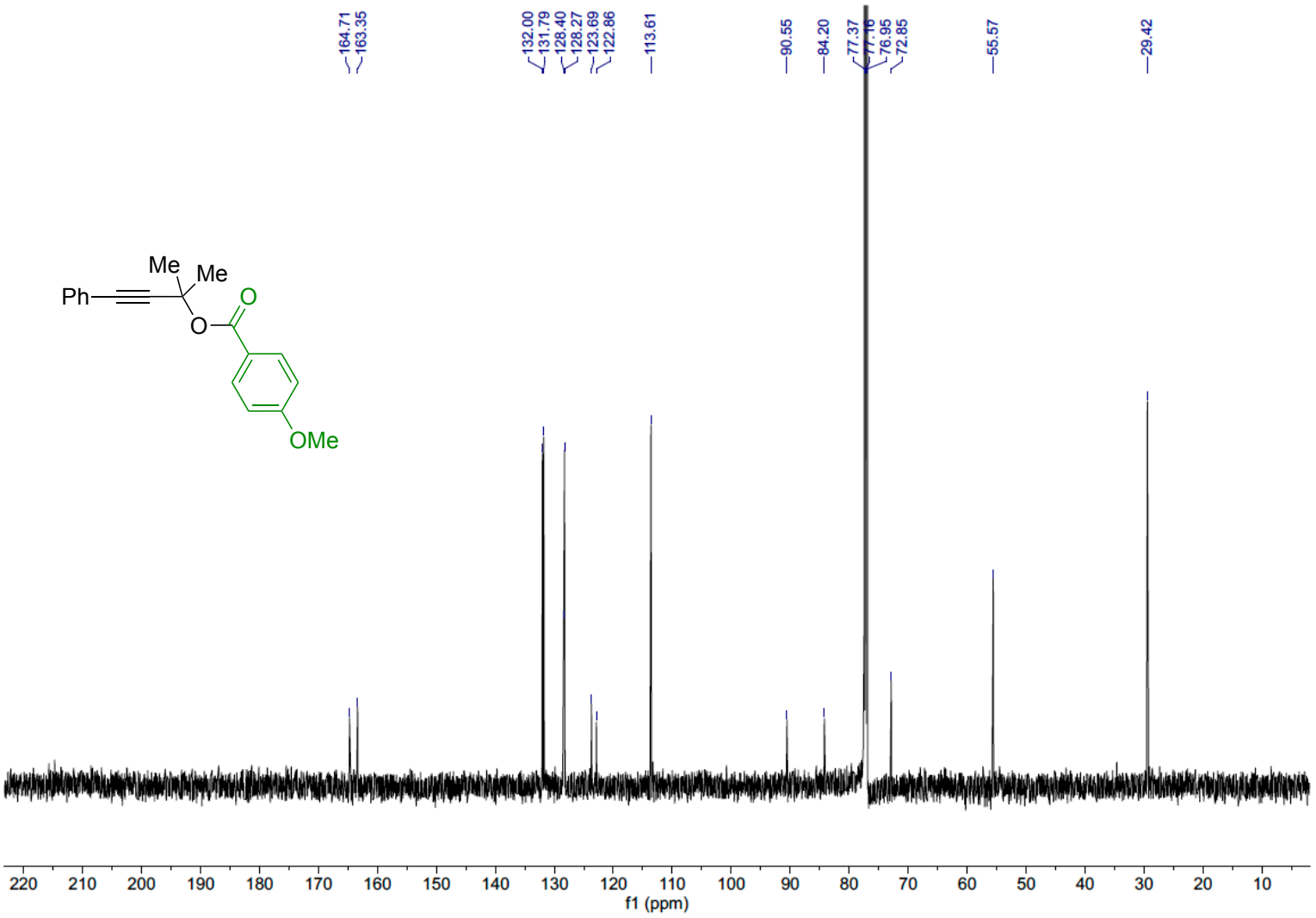
6d

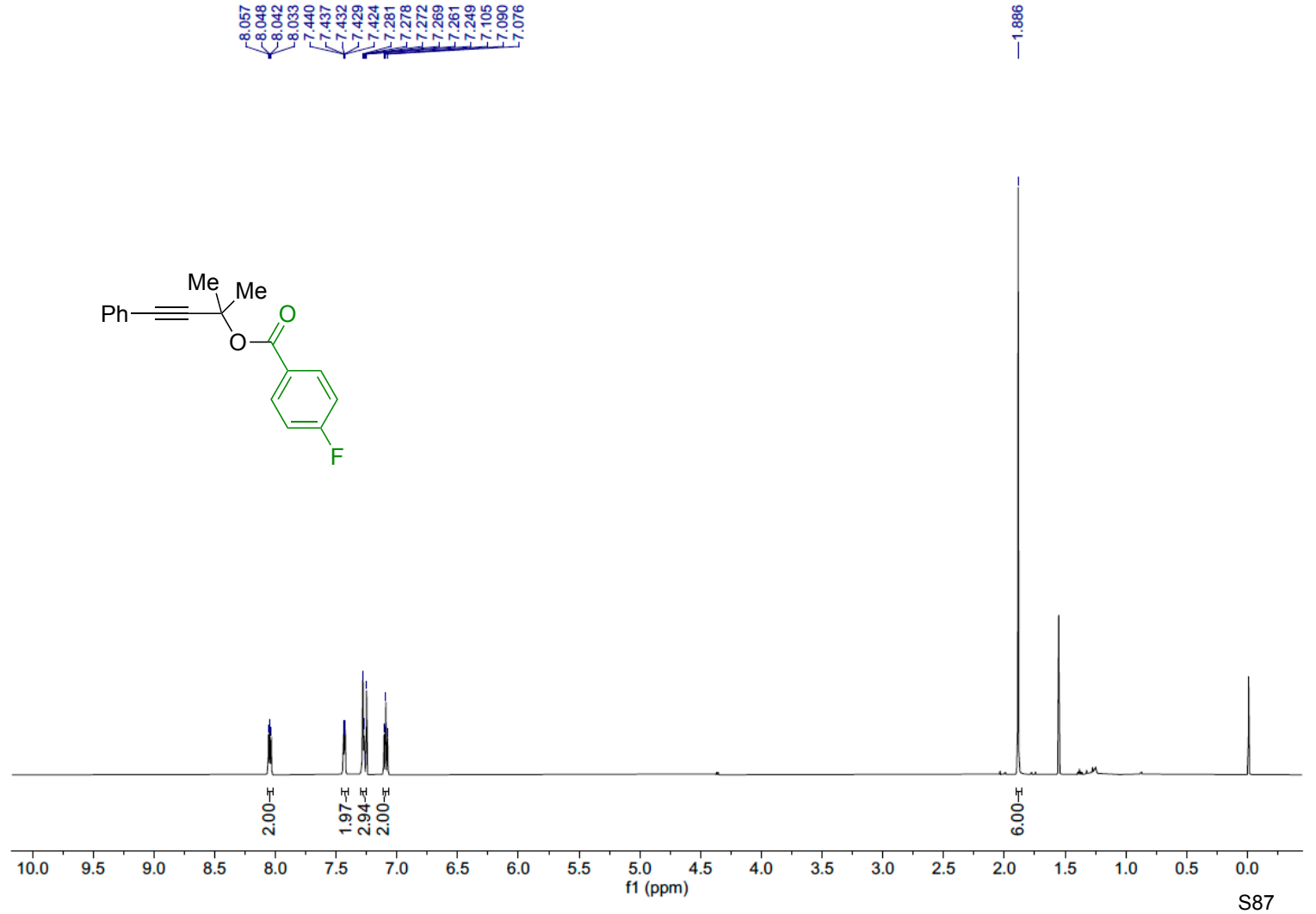

200.42
138.61
137.90
132.52
128.28
128.16
126.08
125.40
123.37
121.27
121.03
118.65
109.67
77.37
77.16
76.95
49.60
34.88
32.68
28.78
O
Me
Me
Ph
N
Me
6d
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

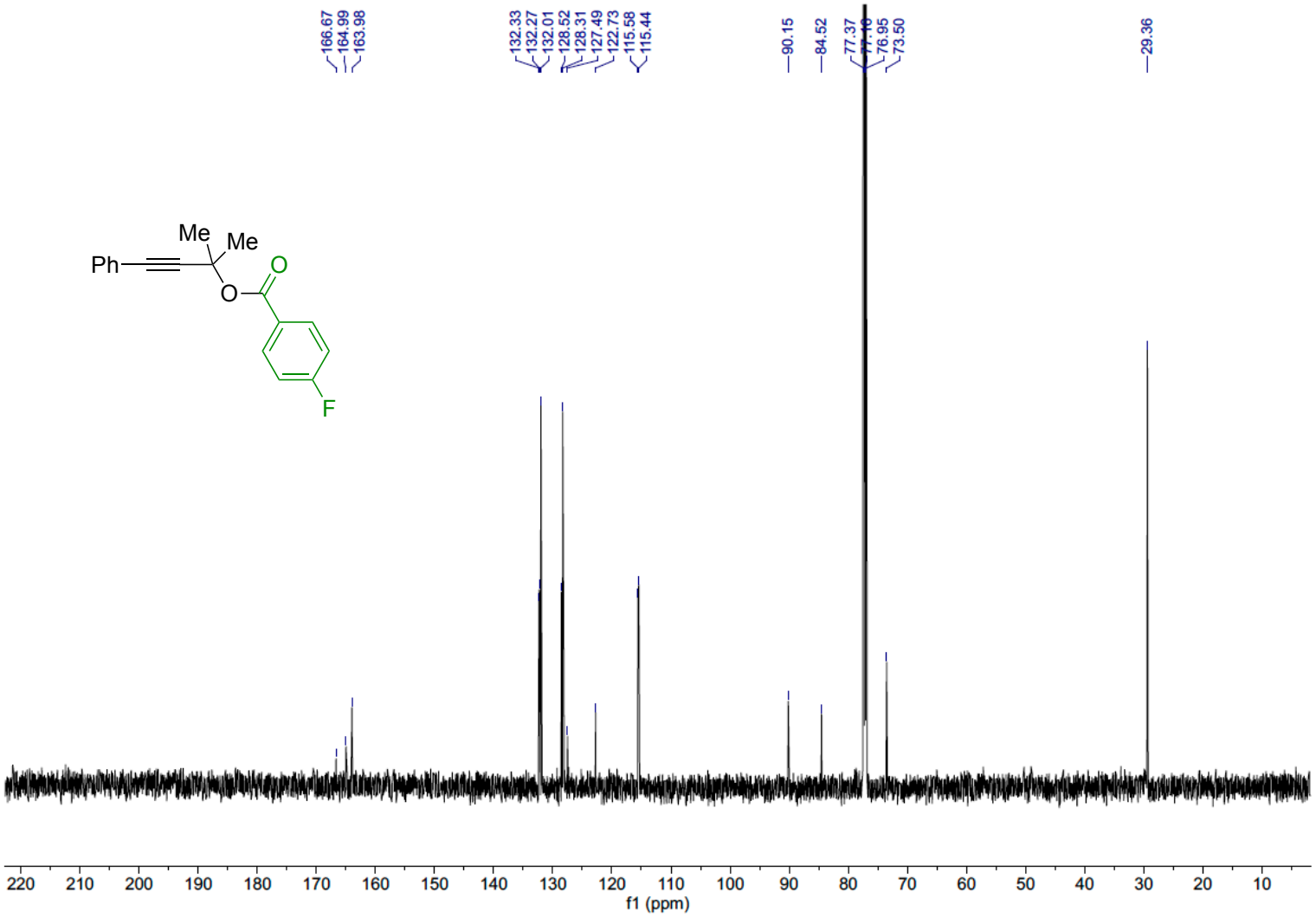

7.260
2.394
2.388
2.380
2.373
2.367
2.358
2.352
1.980
1.741
1.729
1.720
1.713
1.708
1.675
1.670
1.664
1.658
1.654
1.648
1.643
1.639
1.632
1.614
1.480
1.474
1.467
1.457
1.447
1.436
1.430
1.420
1.414
1.405
1.396
1.384
1.312
1.293
1.283
1.273
1.268
1.258
1.252
1.246
1.235
Me
Me
OAc
0.96
3.00
2.08
2.03
6.17
3.03
3.02
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

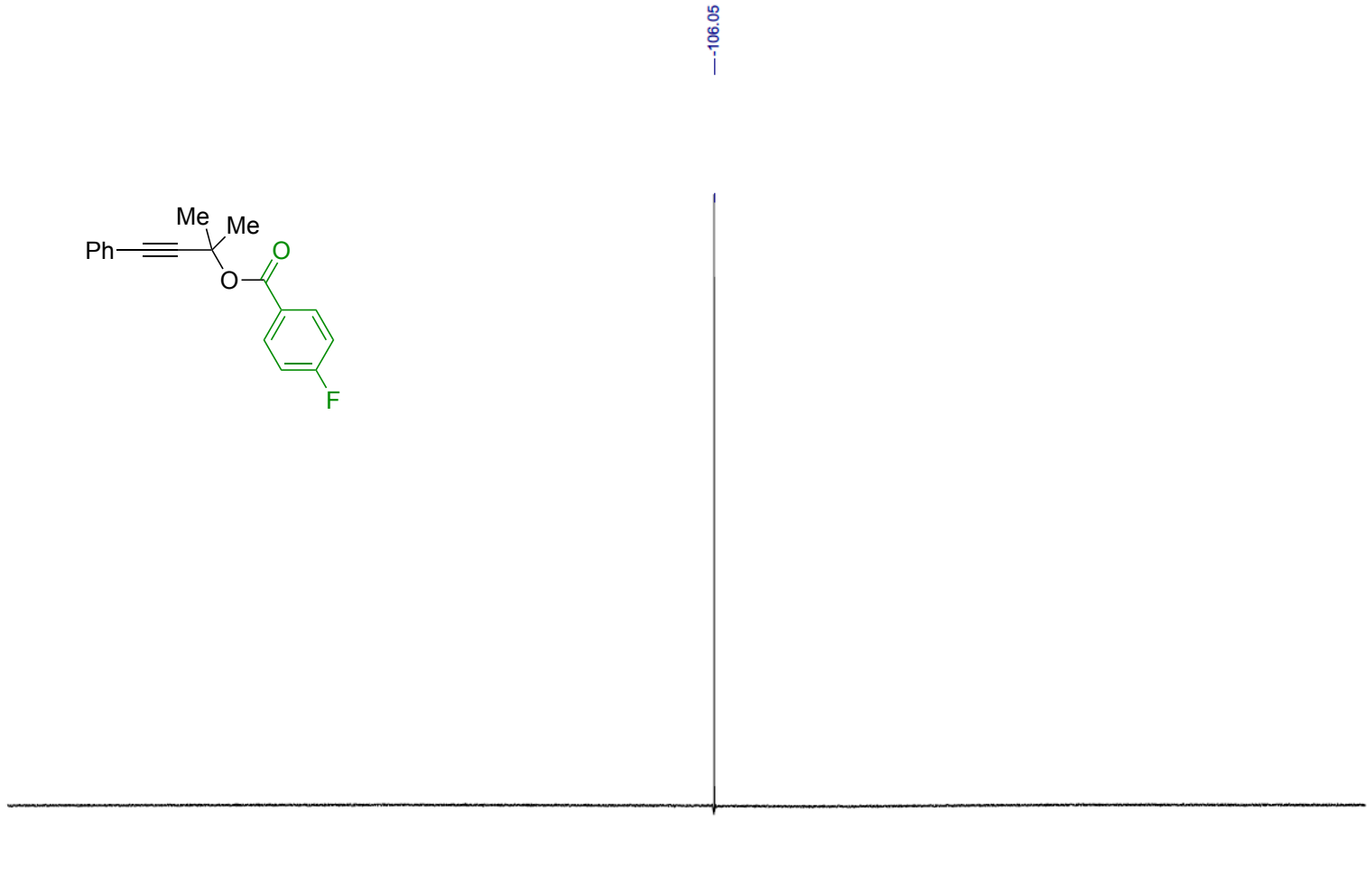

169.47
88.69
81.63
77.37
77.16
76.95
72.78
32.59
29.50
28.94
26.04
24.77
22.27
Me
Me
OAc
f1 (ppm)

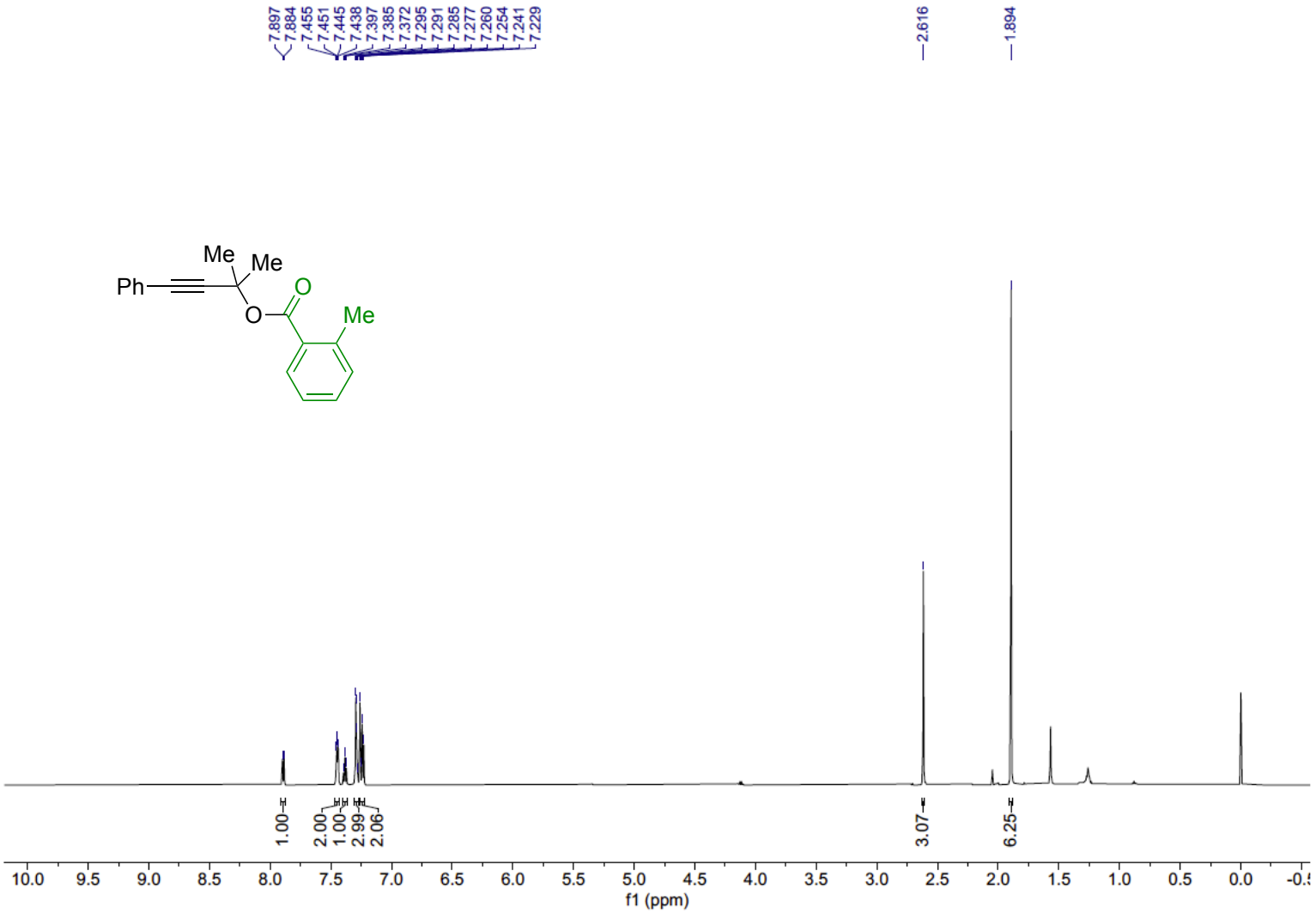

7.993
7.978
7.440
7.436
7.430
7.423
7.273
7.269
7.264
7.249
6.908
6.893
3.848
1.876
Me
Me
Ph
O
O
OMe
2.02
2.00
3.00
2.05
3.10
6.17
f1 (ppm)

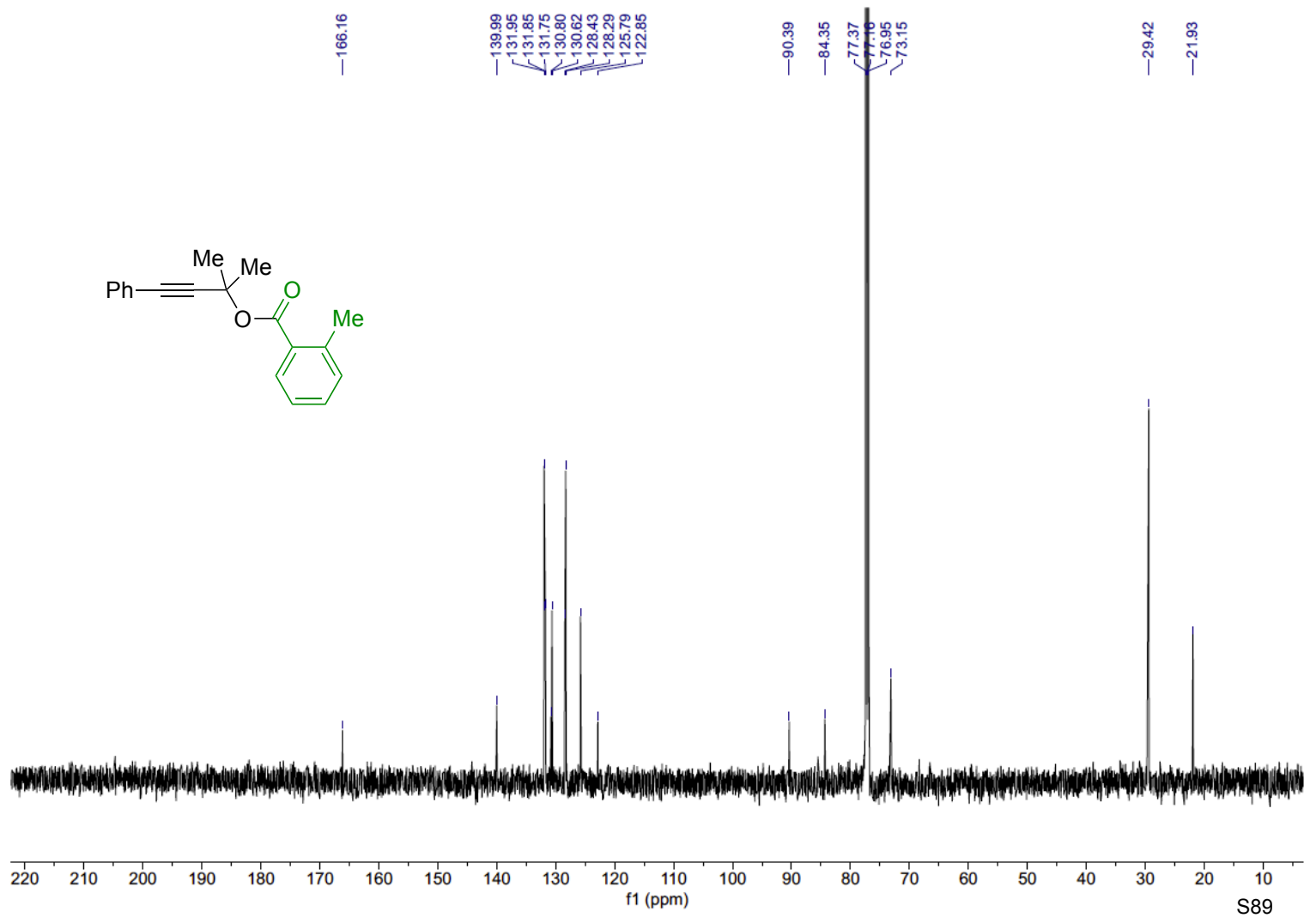

164.71
163.35
132.00
131.79
128.40
128.27
123.69
122.86
113.61
90.55
84.20
77.37
77.16
76.95
72.85
55.57
29.42
Me
Me
Ph
O
O
OMe
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

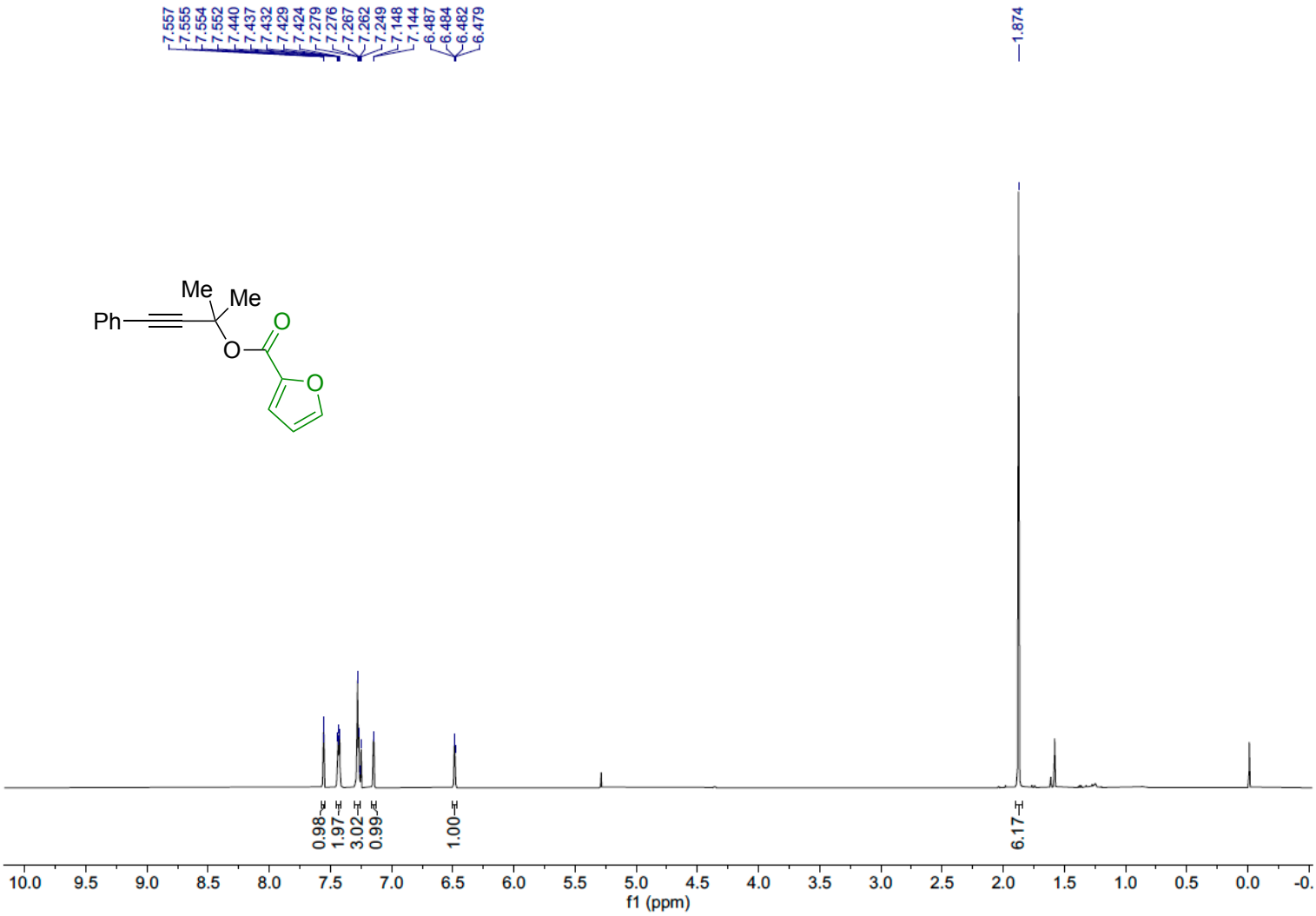

8.057
8.048
8.042
8.033
7.440
7.437
7.432
7.429
7.424
7.281
7.278
7.272
7.269
7.261
7.249
7.105
7.090
7.076
1.886
Me
Me
Ph
O
O
F
2.00
1.97
2.94
2.00
6.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

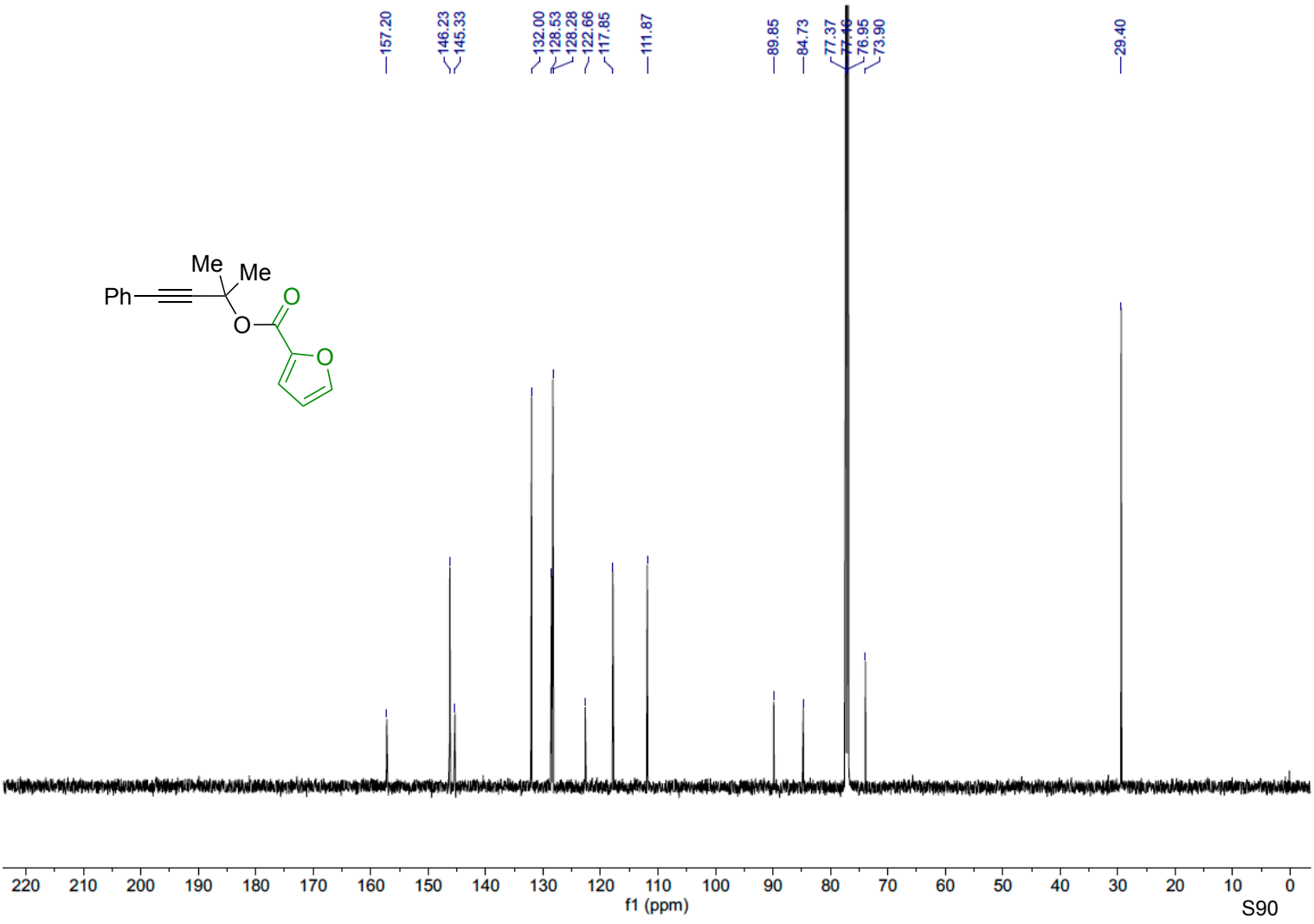

166.67
164.99
163.98
132.33
132.27
132.01
128.52
128.31
127.49
122.73
115.58
115.44
90.15
84.52
77.37
77.16
76.95
73.50
29.36
Me
Me
Ph
O
O
F
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

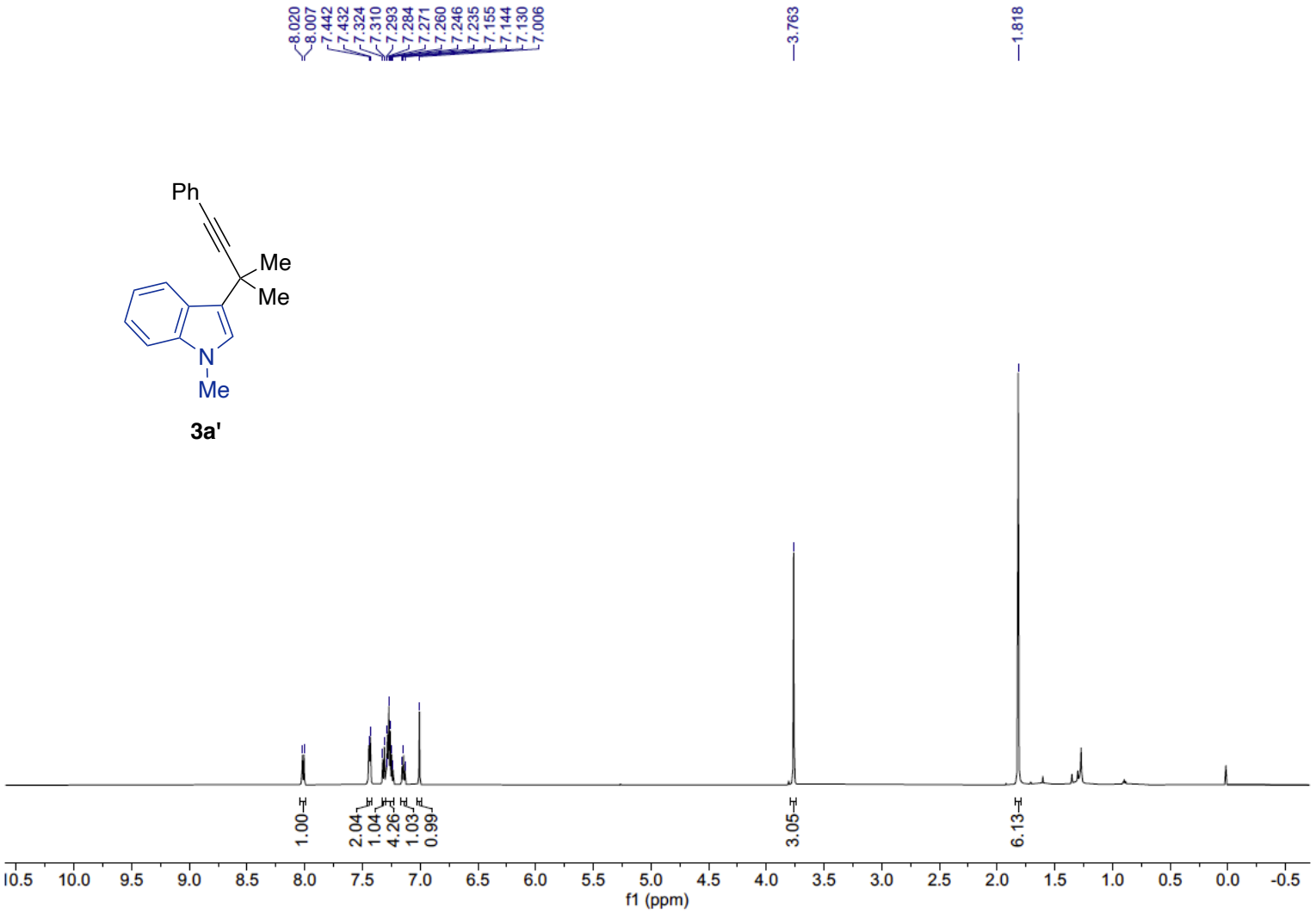

-106.05
Me
Me
Ph
O
O
F
40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240
f1 (ppm)


7.897
7.884
7.455
7.451
7.445
7.438
7.397
7.385
7.372
7.295
7.291
7.285
7.277
7.260
7.254
7.241
7.229
2.616
1.894
Me
Me
Ph
O
O
Me
1.00
2.00
1.00
2.99
2.06
3.07
6.25
f1 (ppm)

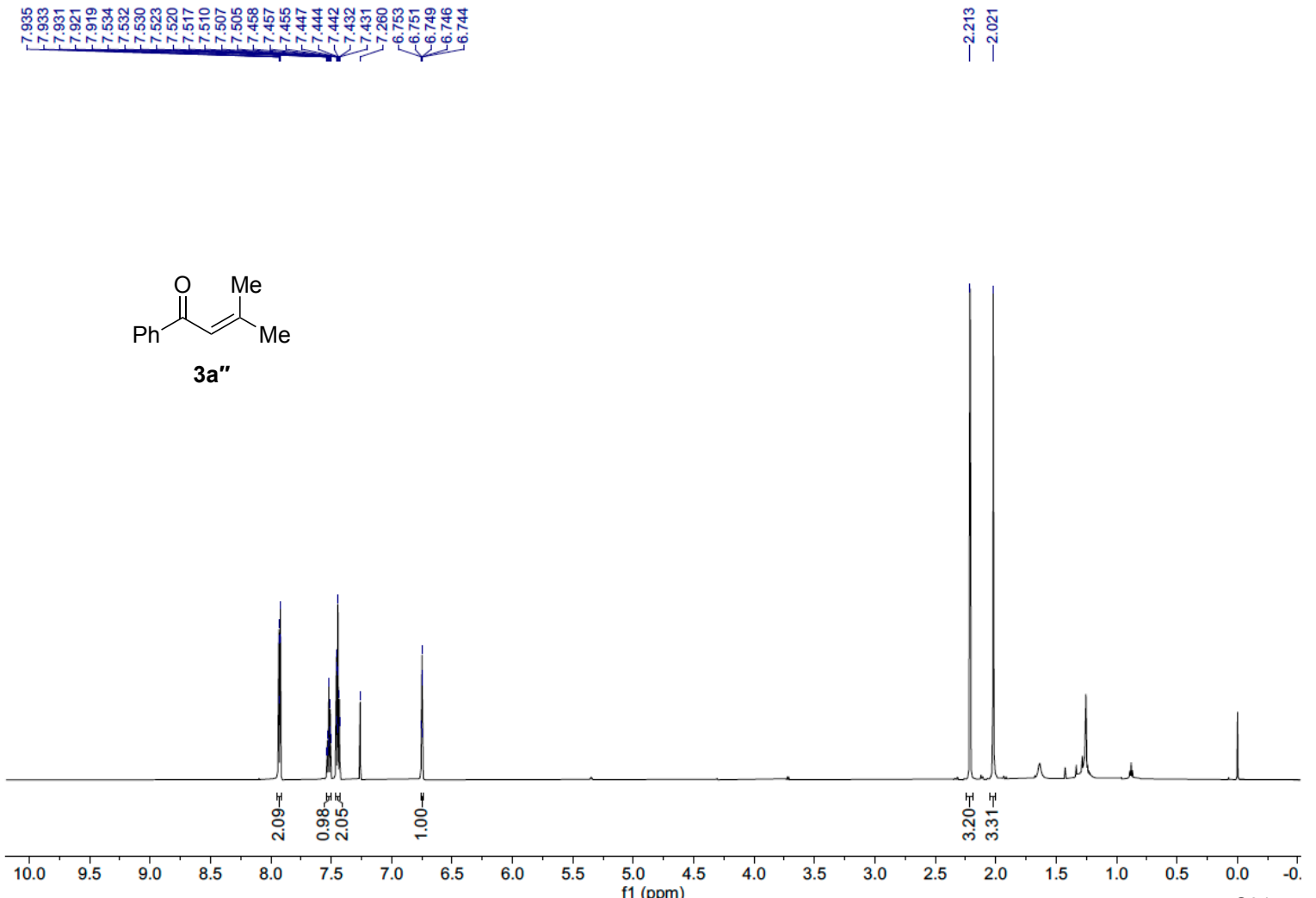

166.16
139.99
131.95
131.85
131.75
130.80
130.62
128.43
128.29
125.79
122.85
90.39
84.35
77.37
76.95
73.15
29.42
21.93
Me
Me
Ph
O
O
Me
f1 (ppm)


7.557
7.555
7.554
7.552
7.440
7.437
7.432
7.429
7.424
7.279
7.276
7.267
7.262
7.249
7.148
7.144
6.487
6.484
6.482
6.479
1.874
Me
Me
Ph
O
O
O
0.98
1.97
3.02
0.99
1.00
6.17
f1 (ppm)


157.20
146.23
145.33
132.00
128.53
128.28
122.66
117.85
111.87
89.85
84.73
77.37
77.16
76.95
73.90
29.40
Me
Me
Ph
O
O
O
f1 (ppm)


8.020
8.007
7.442
7.432
7.324
7.310
7.293
7.284
7.271
7.260
7.246
7.235
7.155
7.144
7.130
7.006
3.763
1.818
Ph
Me
Me
N
Me
1.00
2.04
1.04
4.26
1.03
0.99
3.05
6.13
f1 (ppm)

3a'


7.935
7.933
7.931
7.921
7.919
7.534
7.532
7.530
7.523
7.520
7.517
7.510
7.507
7.505
7.458
7.457
7.455
7.447
7.444
7.442
7.432
7.431
7.260
6.753
6.751
6.749
6.746
6.744
2.213
2.021
O
Me
Ph
Me
2.09
0.98
2.05
1.00
3.20
3.31
f1 (ppm)

3a″